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ON THE USE OF MERCURY THERMOMETERS WITH PARTICULAR REFERENCE TO THE DETERMINATION OF MELTING AND BOILING POINTS.

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The progress made during the last twenty years in the preparation and purification of chemical substances has not been followed by a corresponding improvement in the methods which serve to determine some of their physical properties, and this is particularly true of determinations involving the measure of temperature.

The methods used for the graduation of thermometers are often unreliable, the modes of reading them give varying results, and the ordinary tables of corrections contain errors much greater than those which it is intended to correct.

A series of experiments[1] was undertaken with a view to remedying some of these defects by processes which can be easily carried out in a chemical laboratory, and they were extended to an examination of the best methods of manufacturing nearly accurate thermometers, after it was discovered that the principal defects can be remedied by means easily within the reach of a careful in-

[1] Some of the experiments described in this paper have been published in the Comptes Rendus, **91**, 291, 370, 413, and 574; **94**, 1299, and **95**, 836 and 910. The theoretical considerations of the articles in the Comptes Rendus are here omitted, and a greater development is given to the practical directions concerning laboratory operations. The table of corrections for thermometers with a limited scale has been added.

strument-maker. In fact, the methods of preparation and of graduation of thermometers for higher temperatures, which will be proposed, are similar to the processes now in use for pointing the scale between zero and 100°; and it is hoped that they will insure nearly as great accuracy for the temperatures between 100° and 360° as is now obtained with normal thermometers between zero and 100°.

The different sources of error in the kind of thermometric observations that we are considering will be examined in detail.

Mercury Thermometers.— The Calibration.

The standard thermometers made at the observatory at Kew, and those of M. Baudin, of Paris, are calibrated before graduation in order that the stem may be divided into parts of equal capacities, and a subsequent calibration made with the best apparatus shows residual errors of 0.015° to 0.04°, when the scale is divided in tenths of a degree. The process of correction of the errors of calibration and graduation attains an exactitude 0.002°.[1]

Thermometers made with extraordinary care, and divided into 500 parts between zero and 100 degrees, or into 360 degrees for the complete scale, are found to have a mean error not greater than one-third of a division.

The thermometers ordinarily used in chemical laboratories are far from being equally exact; for instance, 19 French and German thermometers were found to have differences of 0.1° to 0.5° in the length of contiguous sections of 25 degrees. If the tube is regularly conical these differences are cumulative; thus an error of 3.6 degrees at 230° was found in calibrating a thermometer of this kind (the value of the degree between zero and 100° was taken as unity).

Most frequently the variations in the length of a column have sometimes a plus, sometimes a minus sign, but these errors do not usually cancel each other, and it is rare to find ordinary thermometers which do not require at several parts of their scale corrections for errors of calibration amounting to a large fraction of a degree; hence for accurate work the thermometer should be calibrated according to one of the methods described in physical text books.

[1] M. Pernet, of the International Bureau of Weights and Measures at Sèvres, has had the kindness to furnish the details regarding the calibration of standard thermometers.

It is impossible by the ordinary processes to calibrate the thermometers intended for use at high temperatures, when the tube contains air; but the following method gives a sufficiently exact calibration when the upper reservoir is large enough to contain at least $\frac{1}{10}$th of the mercury of the bulb. The bulb is heated until part of the mercury rises into the reservoir and there a globule is separated by a jerk, and by trial a sufficient quantity is detached to make a column of 20 to 30 degrees. The thermometer is allowed to cool in such a manner that this small column follows the mercury in the stem with an interval of 10 to 30 degrees, which space is necessarily filled with air. On account of the air it is impossible by the usual method to change at will the position of the separated column; it follows the main body of the mercury, but it may be fixed without great difficulty at the required points by heating the bulb to temperatures which must remain constant during each observation of the length of the small column. For this purpose a very simple thermostat is employed, consisting of a copper tube about 25 cm. long with the sides 3 mm. thick. The bulb of the thermometer is introduced into the tube, placed horizontally, where it is heated by conduction, and the temperature is regulated by placing the lamp under the tube at the requisite distance from the part containing the bulb of the thermometer. In this way it is easy to maintain a sufficiently constant temperature, because small movements of the main body of the mercury do not usually force the detached column to change its position.

The Value of the Degree.

The first accurate researches in thermometry were made in order to find suitable means of determining the two points which fix the value of the degree, and the necessary precautions for determining the freezing and boiling point are described in the physical text-books. It is important to use a good barometer, which does not require a notable correction for the capillary depression; and in order that the reduction of the mercury column to zero may be exact, the barometer should be sheltered from rapid changes of temperature. This may be conveniently effected as recommended by Professor Rowland, by wrapping the barometer with its thermometer in several folds of flannel. Instead of the boiling apparatus of Regnault, a glass flask with a long neck of at least 6 cm. diameter may be substituted without diminishing not-

ably the accuracy of the determination. In all cases the bulb and the entire mercury column must be heated in the steam.

The thermometer may be inserted through a pin-hole pricked in a thin diaphragm of rubber, so that only a few tenths of a degree need be withdrawn from the steam in order to make an observation. Zinc or copper turnings are put in the water.

It is very important to follow an invariable order in observing the points 100° and zero. The 100° point is observed first, and it is indispensable to make the zero determination immediately afterwards. Instead of allowing the thermometer to cool in the vessel used for the boiling point of determination, it should be taken out quickly, while heated to 100°, and as soon as it has taken nearly the temperature of the air (this requires 5 to 7 minutes) it is plunged into snow which has been for a long time in contact with distilled water. When snow cannot be procured, it is best to substitute ice finely divided by planing it with an ordinary wood plane. This artificial snow may be placed in a cavity at least 5 cm. in diameter, made in a mass of pounded ice, filling a large vessel, which should be provided with means for draining off the water.[1]

Even with the best thermometers it is not common to find that exactly 100° of the scale are comprised between the temperature of steam at 760 mm. pressure (barometer reduced to zero) and the temperature of melting ice. The standard thermometers show divergences of several hundredths of a degree, and thermometers which are made for use in chemical laboratories have errors which are sometimes as high as zero, 0.8° in 100°, which would entail an error of 2.4° at 300°, since all the measures of temperature are divided by the value of the degrees established between 100° and zero.

It is necessary always to follow the method indicated, or at least an invariable matter in determining the value of an interval 100°–zero, since a variation of method may cause this quantity to vary 0.2° to 0.5°.[2]

[1] In all exact determinations the snow should cover a considerable part of the scale, and instead of uncovering the zero at the moment of reading its position, it is preferable to bring this point before the smaller aperture of a conical glass tube, which is embedded in the snow, so that the divisions of the thermometer can be read by looking into the larger end. With this arrangement the scale can be conveniently observed with a telescope furnished with a micrometric eyepiece, the lighting is good, and the air of the tube being cooled to zero, the observation is not hindered by the moisture which is usually condensed on the stem of the thermometer in the ordinary method of making zero point determinations.

[2] The method here recommended has always been followed by certain experimentalists, and M. Baudin has employed for a long time a similar process for the graduation of his thermome-

Even when an invariable method is employed for the observations, important errors may proceed from another cause, which has hitherto escaped attention: the value of the degree itself usually varies each time that a change of position of the zero point occurs, and all the constants of the thermometer are changed in different proportions.

During the ordinary usage of a new thermometer at temperatures above 100° a gradual elevation of the zero point takes place, and the value of the degree changes at the same time. This movement has been followed with seven thermometers made at Paris, of crystal glass containing about 18 per cent. of oxide of lead; and during a series of experiments like those common in chemical laboratories, the following elevations of the zero point and augmentations of the interval 100° to zero were observed simultaneously. The movement was progressive during the whole series of experiments, but only the final variations are given in the table.

Nos. of thermometers	45	46	47	50	52	53	54
Rise of the zero point	2.11°	1.24°	1.36°	2.76°	2.38°	3.39°	2.40°
Increase of the interval 100°– 0°	0.14°	0.06°	0.05°	0.13°	0.10°	0.19°	0.07°

By inducing larger elevations of the zero point the corresponding changes in the interval 100° to zero can be better studied, because certain irregularities are then only of slight relative importance compared with the larger numbers which have to be considered.

The following series of experiments is well fitted to show the magnitude of these changes, and they were also undertaken particularly to test the point whether the changes produced at mod-

ters, but it is only lately that the rule can be considered as established among physicists to take as a point of departure of each measure of temperature the position of the zero point determined immediately after each observation. The best arguments in favor of this mode of proceeding have been given in the excellent memoir of Dr. Pernet, who has shown what confusion arises when the zero point is observed before the determination of temperature. In this last case it is necessary to take into consideration the changes which preceding operations have caused in the position of the zero point, and a minute study of the special qualities of the thermometer is required before the measures taken by different methods can be compared with each other. Dr. Pernet has calculated a series of corrections of this kind for temperature between zero and 100°, and the data will be given further on for making similar calculation in the case of higher temperatures, but only when the zero point at its maximum of elevation is to be dealt with. The observations of several authors lose all value as true measures of temperature from the absence of details regarding the method which they have employed. It is to be noticed that the graduation of instruments at the Kew observatory is still based upon the determination of the zero *before* that of the higher temperature.

erately high temperature were similar in character to those observed after heating to the highest temperatures to which the thermometer can be conveniently exposed.[1]

Nos. of thermometers	1	2	3	4	5
Rise of the zero point	23.0°	24.0°	26.0°	16.6°	11.0°
Increase of the interval 100°–0°	0.9	0.45	0.85	0.50	0.70

Nos. of thermometers	6	7	11	13	15
Rise of the zero point	15.8°	11.7°	9.9°	12.0°	13.7°
Increase of the interval 100°–0°	0.80	0.50	0.94	0.77	1.30

The thermometers Nos. 1, 2, 3, 4, 11, 13 and 15 were made of French crystal glass containing about 18 per cent. of oxide of lead. The Nos. 5, 6 and 7 were of German soda glass. The seven thermometers were heated eleven days at 355°. The Nos. 11, 13 and 15 were heated three years at 166°, 206° and 266°. It will be seen that similar effects are produced at these relatively lower temperatures and at the highest, and no known fact justifies the opinion of several authors that the phenomena which take place when glass is heated change their character at the different temperatures within the above range. Even at 100° by prolonged heating an augmentation equal to about 0.05° of the interval 100° to zero may be produced, while the position of the zero point is raised by some tenths of a degree.

Thus after any change in the position of the zero the interval of 100° to zero must be determined anew, and usually a new value for the degree will be found by which all the measures of temperature must be divided. But measures thus corrected will probably not stand in a simple relation with the old ones, and after each considerable change of the position of the zero point the thermometer should be again compared with the air thermometer throughout

[1] Dr. Pernet (Comptes Rendus **91**, 471) had stated his opinion that no variation of the interval of 100° to zero is produced when the heating takes place at temperatures not higher than 100°. According to my experiments a variation of the interval must always be looked for when the position of the zero point changes, and under certain conditions a constant relation may be observed between the amplitudes of these two movements. I have given (Comptes Rendus **91**, 574) an hypothesis which may serve as a guide to the study of this phenomenon, but I do not propose here to discuss theoretical views, nor to enter into the details of certain experiments which were suggested by them. In this paper it is intended only to discuss the side of the question which is practically more important: namely, the possibility of obviating this source of error. The means by which this result may be effected will be described in full. They consist in a preparatory treatment of the thermometer which serves to make the position of the zero stable within certain narrow limits, and at the same time the value of the degree becomes practically unalterable.

the whole length of its scale in order to establish a new series of corrections.

It will be thus seen that this phenomenon has a most disastrous influence upon the precision of thermometric measurements, and it is important to examine into the causes of these movements and to endeavor to find means to suppress them.

Depression of the Zero Point.

Let us consider the case of a thermometer which has been brought by special treatment to what may be called its normal condition at the ordinary temperature. This is effected by causing the disappearance of certain persistent and abnormal expansion of the glass by heating a very long time (several days at 355°) and by cooling very slowly (during several weeks). When such a thermometer is heated successively at a series of different temperatures, each higher than the last, and after each heating cooled immediately in the air and the zero point observed, a depression of zero is found to correspond with each successive heating at the increasing stages of temperature, and the extent of the depressions rises in a more rapid ratio than the temperatures of the heatings to which they correspond.

It is a well-known fact that the extent of the depression depends upon the manner in which the thermometer is cooled to the ordinary temperature; for example, after heating to 100°, if the thermometer, instead of cooling directly in the air for 5 to 7 minutes, is taken from the heating apparatus and plunged immediately into a series of baths regulated at 60°, 30°, etc., it can be brought to the temperature of melting ice in one or two minutes, and in this case the position of the zero is about 0.05° lower than in the first case. This process of rapid cooling by means of baths is employed by M. Baudin, and consequently the interval of 100° to zero on his thermometers is greater by 0.05° than it is found when determined by the method recommended in this paper.

If the thermometer is cooled as slowly as possible during twenty-four hours after having been heated to 100°, the position of the zero is about 0.15° higher than when it is cooled in the air, and the position of the zero point is raised about 0.15° still higher when the thermometer is cooled slowly and methodically during a period of several weeks. It is evident that each way of operating would give a different value for the degree.

The method which has been recommended above gives values for the interval 100° to zero which are constant to about one hundredth of a degree.

The first vertical column of the table contains the numbers designating six thermometers of which No. 5 is made of soda glass, the others are of crystal containing about 18 per cent. of oxide of lead. The remaining columns give the depressions corresponding with the temperatures to which the thermometers have been heated.

It is to be noted that the time required to produce a maximum depression varies with the temperature. At 60° it requires several days, at 100° a few hours, and at the highest temperature from ten to fifteen minutes. The position of the zero at the maximum of depression remains constant on successive heatings at the same temperature.

Table of Zero point Depressions.

Temperatures	40°	60°	80°	100°	160°
No. 1	0.00°	0.06°	0.19°	0.31°	0.74°
5	0.04	0.08	0.18	0.29	0.56
13	0.02	0.03	0.17	0.31	0.69
15	0.01	0.05	0.18	0.31	0.75
31	0.02	0.06	0.22	0.37	0.84
32	...	...	...	0.28	0.69

Temperatures	218°	260°	306°	355°
No. 1	1.12°	1.33°	1.63°	2.19°
5	0.76	0.91	1.14	1.51
13	0.87	1.09	1.30	2.15
15	0.97	1.12	1.40	2.05
31	1.15	1.46	1.77	...
32	0.98	1.21	1.56	2.06

This table may be used in the following manner to compare observations made by different methods. Suppose, for instance, that a temperature has been measured by the method which was chiefly used formerly, the zero point was first taken, and then a series of rising temperatures was observed, as for example 100°, 200° and 300°. The same observations referred to a zero point determined immediately after each one will give the measures 100.3°, 201.0° and 301.5°, if the depressions had been the same as the thermometer No. 1 in the table. All these last observations are to be divided by 1.003, which is the value of the degree

in this case, and thus the second method would give 100°, 200.4° and 300.6° instead of 100°, 200° and 300°. The table of corrections to reduce the scale of mercury thermometers to that of a gas thermometer is founded on the assumption that the last method of observation has been employed; and consequently when any other method is used, additional corrections like those above must be applied, and the rate of the zero point depressions under the circumstances of the experiments must be known.

The preceding calculations are only applicable to the cases in which the zero point has completely returned to its normal position at the commencement of a series of experiments, and also the successive heatings must take place at increasing temperatures. Very often the depression of the zero produced by the preceding experiments still persists at the commencement of a new series, and in that case, instead of observing a depression on heating, a rise of the zero point is to be noticed, and a knowledge of the laws regulating the elevation of the zero is required to calculate its position in such an experiment. It will be seen that the relations between the measures made by different systems may become extremely complicated, and it is to avoid difficulties of this nature that an invariable method has been recommended, viz. that which takes for the point of departure of each measure the position of the zero determined immediately after each observation of temperature.

The Rise of the Zero Point.

After a depression of the zero point, if the thermometer is left at the ordinary temperature, the zero is found to gradually rise through a tendency to return to its original position,[1] and the study of such movements as may be produced by exposing a thermometer during a very long time to constant temperature gives the data for calculating the position of the zero point under all circumstances, and what is more important, the study of this question

[1] I have followed this movement under varied conditions in order to ascertain if it is regular, *i. e.* if the experiments can be so arranged as to give identical results under conditions which appear to be similar. In more than 1000 observations the divergences which escape a control of this sort do not appear to exceed 0.02° to 0.03°, but it would be very difficult to find a general formula for a movement which not only depends upon the time but also upon the temperature, and it must also be remembered that the depressions whose disappearance constitutes the phenomenon to be observed are often due to successive heatings at various temperatures, and represent the accumulation of several different impulses.

Mr. Mills in a general formula for the rise of the zero point at the ordinary temperature appears to have taken into account no factor except the time.

leads to the discovery of the means for preventing those variations of the constants of a thermometric scale which are fatal to the precision of all measurements. It is particularly from this point of view that we are interested in the subject, and only those details will be given which have a direct bearing upon improvements in the manufacture of thermometers.

If after a depression produced by heating a thermometer is heated at a lower temperature, the zero point tends to gradually return to the position which is normal for this last temperature. The complete return or rise of the zero is more rapid in proportion as the temperature which produced the depression is not far removed from that which brings about the rise. The time required for this movement is measured by hours at the highest temperatures and for small intervals (10° to 20°), and by days or months at lower temperatures (100° or the ordinary temperature). When the interval is very large a part of the depression produced at a high temperature is permanent at the lower temperature. Thus a thermometer heated at 355° may be left for an indefinite period at the ordinary temperature without showing a rise of the zero equal to more than one-half of the true depression, but this depression may be made to disappear entirely when the thermometer is heated methodically for several days at each of the temperatures 300°, 250°, 200°, and so forth, to the ordinary temperature.

When a new thermometer is heated during a week or ten days at 355° a very considerable rise of zero is noticed. In the case of soda glass the zero may rise 10° or 15°, and with crystal glass 15° to 26°. This movement is probably the return from a depressed position, like those which have been previously described, and it may be assumed that the depression of the zero or the abnormal expansion of the glass was produced during the operation of blowing the bulb of the thermometer, and that it has resulted from the rapid cooling of the glass while still soft. Moreover, as it has been seen that the depressions of the zero point produced at 355° or 300° persist at the ordinary temperature, so also this abnormal expansion produced at a red heat is permanent at low temperatures. And it is in accordance with the rule derived from the previous results that the abnormal expansion should disappear when the thermometer is heated to a temperature nearer to that which produced the expansion. Thus the extraordinary rise of the zero point which may be produced by heating to 355° or higher temperatures

is probably almost entirely due to the same causes which induce the permanent elevation of the zero point at the ordinary temperature, and the effects which previous observers have attributed to the pressure of the atmosphere are really due to an interior transformation[1] of the glass, almost or quite independent of external pressure. Thus similar results are obtained with vacuous or air-filled thermometers, and the progress of the changes, which have to do almost exclusively with the duration of time and the temperature to which a thermometer of a given kind of glass is exposed, is entirely under control.

Let us examine the rapidity of the change at different temperatures. The rise of the zero point in a thermometer which is kept at the ordinary temperature becomes continually slower, and ceases to be appreciable after five or ten years. Thermometers have been observed for more than two centuries, and even after this great lapse of time the displacement of the zero is not more considerable. It usually attains about one-half a degree. In the same way the rise of the zero which is produced by heating to any fixed temperature tends to reach a limit, and the whole movement appears to be more rapidly completed the higher the temperature. On heating to 355°, after ten days, without having reached the limit, the thermometer may be considered as having become virtually stable, since the movement of the zero point has become so slow that no noticeable displacement is produced during any ordinary experiments of short duration, even when the heat is carried as high as the boiling point of mercury, and such a thermometer may be heated several days at 300° or 200°, or several months at 100°, or it may remain several years at the ordinary temperature without alteration to the effect produced at 355°. By this is meant

[1] Dr. Löwenberg (Berichte chem. Gesell. **10**, 472) supposes that the particles of glass after heating are in a state of tension produced by the slight conductibility of glass, which occasions a cooling or setting in successive layers, and that this abnormal tension may disappear in consequence of oft-repeated molecular movements.

I am unable to estimate the consequences which follow upon this manner of considering the phonomena, but the following experiment was suggested by M. Dufour's observations upon rapidly cooled glass drops. He found that these drops contain a vacuous cavity, and consequently that after the solidification of the outside layer the interior mass must solidify under a diminished tension. It occurred to me to examine whether the exterior layer of the bulb of a thermometer exercises mechanical pressure on the interior layers: the result was negative. A large thermometer, newly made, was left in hydrofluoric acid until about one-third of the thickness of the bulb was dissolved, and no considerable change in the position of the zero took place. Care was taken to open the stem before the experiment in order to guard against the effect of the pressure of the atmosphere upon the bulb, made thinner by the action of the hydrofluoric acid.

that, although certain slight elevations take place at lower temperatures such as those which have been previously described, yet, whenever the thermometer is heated again to 355°, the zero point immediately returns to the position which it had after the first prolonged heating in boiling mercury. It may be concluded from what precedes that the extreme variations of the zero point to be observed with what has been called a stable thermometer, are comprised within limits of about 2° between the point of extreme depression for 355°, and a complete return to the higher position corresponding with the ordinary temperature, and the table of depressions gives the point within these limits to which the zero may be brought and permanently fixed by heating at any constant temperature.[1] Similar series of observations were made with exactly similar results when, instead of 355°, the highest limit of temperature was fixed at 300°, 260°, 200° or 100°.

It will be seen that only thermometers that have thus been made stable can be used where the position of the zero is to be determined by calculation, and what is more important it is that only with such instruments is the value of the degree constant, and that with constant thermometers any table of corrections obtained by comparison with an air thermometer remains permanently applicable. It may be added that the curve of corrections for thermometers that have been so heated as to produce the largest displacement of their zero point does not vary in form from the curves of corrections to be applied to new thermometers to bring their scale into accordance with that of a gas thermometer. Five of the thermometers which were used in my experiments to compare the mercury with the hydrogen thermometer were subjected to a prolonged treatment at high temperatures, and the curve of average corrections obtained with these five instruments was found not to differ essentially from the average corrections determined from the other thermometers.

The Preparation of Thermometers.

The conclusions to which the preceding paragraphs lead may be summed up in a few general directions for rendering thermometers unchangeable. Those which are intended for the ordi-

[1] This statement must be taken in conjunction with what has been previously said concerning the persistency of depression for long intervals of temperature, and the appropriate means of making them disappear.

nary experiments between zero and 360° should be heated throughout the whole length of their stem for a week or 10 days in boiling mercury, and the graduation, the determination of 100° and zero points, and the calibration, should be made after this treatment; they then acquire a permanent value. When the scale only extends to some lower temperature, 200° or 100°, the time required for the preliminary treatment is proportionally longer. To prepare a standard thermometer for use at temperatures between zero and 100° it should be heated throughout its length for several weeks at 100°, or the process may be shortened by heating it in essence of turpentine at about 156° for four days and then for a week at 100°.

The thermometers must not in any case be subjected for a long time to the action of water, and all these operations can be most conveniently carried out with a metallic apparatus, which is similar to that described further on for fixing accurately certain temperatures, except that many of the precautions there recommended for avoiding slight variations may be omitted. A cylindrical vessel of copper or iron with an hermetically fitting cover communicates with the air by means of a tube, upon which is fixed a condenser, so that evaporation is prevented and the heating at a constant temperature may be prolonged for any length of time. The thermometers are placed in an interior tube closed at the bottom and fitted into the cover with a perfectly tight joint. All the joints are brazed when the apparatus is made of copper. They are fitted by grinding and sweating on when the apparatus is made of iron. These pieces of apparatus have been found most convenient for heating sealed tubes or for any laboratory work where a fixed temperature is required. By the use of several substances, boiling under varied pressures, any temperature can be maintained constant for days or months to within one-fifth degree. They require no attention to regulate temperature, they are quickly heated and cooled, and if the sides are properly protected by a non-conducting jacket they are much more economical of gas than any oil or air bath used for similar purposes. This mode of maintaining fixed temperatures, which was first studied by Regnault, cannot be too highly recommended for laboratory work.

A tight-fitting apparatus for boiling mercury is difficult to construct, and when it is only to be used to prepare "constant" thermometers for graduation (but not to graduate them), it suffices to use an iron tube closed by welding at the bottom, 5 or 6 cm. wide and one metre long, filled with mercury to a height of 5 cm. This

lower portion is heated directly over the lamp. A non-conducting jacket protects a length above this of 60 cm., and the mercury condenses in the upper part of the tube, which is exposed to radiation. Or in case mercury fumes are to be feared, the upper end of the tube can be surrounded by a condenser. The thermometers are enclosed in a sealed glass tube. A similar form of apparatus has been found most convenient for boiling sulphur and other substances in Victor Meyer's vapor density determination.

Corrections to be applied to the results obtained with the Mercury Thermometer to bring them to the true temperature as measured by a Hydrogen Thermometer.

Each mercury thermometer has its individual scale requiring somewhat different corrections, but since the publication of Regnault's memoirs it has been customary to distinguish two categories of thermometers according as the glass is crystal containing oxide of lead or is ordinary glass. The columns A and B in the table below contain the corrections of Regnault for crystal glass from the manufactory of Choisy-le-Roy, containing 34 per cent. of oxide of lead, and for ordinary French glass.

Neither of these kinds of glass is now used to make thermometers. The crystal which is employed at Paris contains about 18 per cent. of oxide of lead; the German soda glass is free from lead, but it is much more fusible than ordinary French glass, hence a revision of these tables has become necessary. The column C of the table was obtained by experiments with 14 crystal glass thermometers made at Paris, and with a soda glass thermometer made at Bonn. To use the table the number of degrees centigrade is read off on the mercury thermometer, the position of the zero is determined immediately afterward, and the correction if necessary is made for its displacement; then the corrections of the table, observing their signs + or —, are added to the numbers of degrees thus obtained, and give the temperature which would have been found by a hydrogen thermometer, supposing that the calibration and the interval 100° to zero of the mercury thermometer are exact.

Tempera-tures,	110°	120°	130°	140°	150°	160°	170°	180°
A . .	—0.05	—0.12	—0.20	—0.29	—0.40	—0.52	—0.65	—0.80
B . .	+0.02	+0.05	+0.09	+0.15	+0.20	+0.26	+0.32	+0.37
C . .	+0.02	+0.04	+0.09	+0.16	+0.25	+0.33	+0.35	+0.34

Temperatures, 190°	200°	210°	220°	230°	240°	250°	260°
A . . −1.01	−1.25	−1.53	−1.82	−2.16	−2.55	−3.00	−3.44
B . . +0.35	+0.30	+0.25	+0.20	+0.15	+0.10	−0.05	−0.20
C . . +0.32	+0.27	+0.18	+0.08	−0.02	−0.14	−0.26	−0.39

Temperatures, 270°	280°	290°	300°	310°	320°	330°
A . . −3.90	−4.48	−5.10	−5.72	−6.45	−7.25	−8.22
B . . −0.38	−0.52	−0.80	−1.08	−1.45	−1.80	−2.40
C . . −0.50	−0.63	−0.88	−1.21	−1.60	−2.03	−2.48

The immediate measures made with the thermometers referred to in the above table were corrected for errors of calibration and for errors in the value of the degree. This latter correction should always be made after determining the number of degrees corresponding with the interval 100° to zero, and the previous remarks upon the errors of calibration show how far it is necessary to take these into account in ordinary thermometric work. It will be seen that the corrections of the column C do not differ greatly from those found by Regnault with ordinary French glass, but are widely different from those of the column A.[1]

In my experiments the curves which represent the corrections for each thermometer show greater departures from the mean curve C as the temperatures increase, but the greatest differences found were only 0.3° at 200°, 0.5° at 300°, and 0.8° at 330°. These figures represent the extreme errors which are probable on using the column C to correct results with thermometers made at Paris. The German thermometer was not among those which showed the greatest divergence, so that the column C may be considered as applicable to soda glass thermometers, but some experiments made with a number of German thermometers induce me to believe that their average corrections should be slightly lower than those of the column C.

Thermometers with a Limited Scale.[2]

Thermometers of this kind have been frequently used within the last few years to meet the difficulty of heating the entire mercury

[1] It is not probable that these differences are to be attributable entirely to the composition of the glass, and in a paper published in the Comptes Rendus, 6 Nov. 1882, I have pointed out certain features of Regnault's method of operating which lead me to suppose that his corrections are too high.

[2] Thermometers of this kind made at Paris give the zero point and temperatures commencing with about 10°, 20°, 100°, 150°, and so forth. In Germany, thermometers are much used which have the bulb only partially filled and whose scale runs from 98° to 360°.

column, and it is generally recognised that it is inexpedient in ordinary experiments to attempt to make a correction for the portion of the scale which cannot be heated. Thermometers with a short scale have a reservoir blown in the glass about 1 cm. above the bulb in order to contain the mercury corresponding to the number of degrees that it is intended to suppress. The total length of the useful part of the scale is about 15 cm., but it is advisable to prolong the stem some 15 cm. more for the convenience of fixing the thermometers in a boiling apparatus.

This mode of construction has some disadvantages which it is most important to remedy, since thermometers of this kind are the only ones which should be applied in accurate work at high temperature.

1. The rise of the zero point is particularly hurtful because the mercury at zero eventually stands in the reservoir and the verification of the zero point becomes impossible. These thermometers should always be subjected to the preliminary treatment which has been described in order to prevent the rise of the zero point.

2. The determination of the fixed points which limit the scale of these thermometers (for example the points 200° and 300°) has hitherto been made by methods far less accurate than those which are used for determining the points zero and 100°. If the constructor has determined these points by comparison with a standard thermometer in an oil bath, errors of 5° are not uncommon, and much larger ones have been noticed. The only expedient which suffices to give results which can be compared with those obtained by observing the boiling point of water and the melting point of ice, consists in using a similar method for high temperatures. I have not succeeded in finding any melting points constant enough for this use, but the boiling points of several pure substances can be employed like that of water. Geissler introduced several years ago the use of naphthalene[1] for this purpose, and this step is a most important improvement; but he does not appear to have determined the boiling point of naphthalene with an air thermometer, and the temperature which he gives is about one degree too low.

After having examined a great number of substances boiling

[1] Dr. Geissler was kind enough to send me some of the naphthalene which he was in the habit of using, and I found it quite pure. The lower boiling point which he has given is not necessarily in error, if the determination was made with a soda glass thermometer, because such an instrument might really give at 218° about 0.5° lower than the air thermometer, and an imperfection in the boiling apparatus used would easily account for the remainder. Geissler's thermometers do actually mark about 1° too low at this temperature.

between 150° and 360° I have only found two that unite all the qualifications which fit them for this use; they are naphthalene and benzophenone.[1]

It is not necessary that these bodies should be absolutely pure, provided the impurities do not affect the boiling point, and some criterion can be established to mark the requisite degree of purification. It was found that the boiling point of commercial naphthalene did not vary more than 0.10° when it had been purified by any method (chemical or physical fractional distillation or crystallisation) until the melting point was brought to 79.9°–79.6°.

The same is true of benzophenone prepared by means of oxychloride of carbon, when it is purified until its melting point is at 48.0° to 47.7°. It will be seen that considerable limits can be tolerated in the melting points without an equal change in the temperature of the boiling point; in other words, the common impurities cause the melting point to vary, while they have nearly the same boiling point. This quality was regarded as indispensable for the use in view, and it was found necessary to reject diphenylmethane and other substances because they do not fulfil this condition. Bodies like essence of turpentine, which are capable of isomeric changes on heating, alcohols which absorb or give off water, ethers which are decomposed by moisture, as well as most acids, chlorides and similar bodies, are unfitted for the purpose.

[1] A mode of preparation of benzophenone, which was given by Friedel, Crafts and Ador (Comptes Rendus **85**, 672), renders the preparation of this substance possible on a large scale and with the necessary purity. The details of the process will be given elsewhere, but it may be well to indicate one or two points which show that it can be applied without difficulty in a manufactory of chemical products. Oxychloride of carbon is made to act upon benzene in the presence of chloride of aluminium. No difficulty is found in regulating the supply of carbonic oxide when the gas is passed first into a large floating gas-holder containing 50 litres; very simple means suffice to mix in equal volumes chlorine and carbonic oxide, and if the mixture is well made there is scarcely a limit to the rapidity with which it may be passed through a large apparatus in bright sunlight. Three glass balloons of 10 mm. capacity each were used, and the combination takes place chiefly in the first with a considerable evolution of heat. In diffused light the current of the two glasses must be relatively slow.

When carbonic oxide has been used in slight excess the product frequently contains no free chlorine, and in any case an excess of chlorine may be conveniently removed by passing the product into a fourth balloon containing a little benzene exposed to the sunlight. Under the circumstances this absorbent for chlorine is more convenient than zinc or antimony; the rate of formation of oxychloride of carbon can be estimated by condensing it in benzene cooled first with ice and then with a freezing mixture. 100 grams an hour can be obtained with great regularity, and the chloride of aluminium can be subsequently added to this mixture, or the oxychloride of carbon can be passed directly into benzene to which 25 per cent. chloride of aluminium has been added. When the benzene used has been purified by distillation or by fractional crystallisation until its melting point is above 4.5°, the crude benzophenone contained in the reaction is almost pure. It varies only about ½ degree in its boiling point, and the subsequent complete purification is easy.

A primary requisite for this purpose is stability on heating. That of naphthalene is well known, and the inalterability of benzophenone, when boiled for 10 days even under pressure, was tested with perfectly satisfactory results. The vapor density of benzophenone is normal even at a red heat.

The boiling points of pure naphthalene and benzophenone were determined with great care by means of the hydrogen thermometer under pressures varying from 85 mm. to 1800 mm. and a formula found representing their vapor tension. These results, which will be described elsewhere, give the means for heating at will to any fixed temperature between 100° and 360°.

It will be sufficient for our present purpose to give in the following table the boiling points of these two substances under the ordinary atmospheric pressures.

Vapor Tensions.

Naphthalene.		Benzophenone.	
Temperature.	Millimetres.	Temperature.	Millimetres.
215.7	720.39	303.7	723.95
215.8	722.05	303.8	724.77
215.9	723.69	303.9	726.29
216.0	725.34	304.0	727.80
216.1	727.00	304.1	729.33
216.2	728.65	304.2	730.86
216.3	730.31	304.3	732.38
216.4	731.98	304.4	733.92
216.5	733.65	304.5	735.45
216.6	735.32	304.6	736.98
216.7	736.99	304.7	738.52
216.8	738.67	304.8	740.06
216.9	740.35	304.9	741.60
217.0	742.03	305.0	743.14
217.1	743.72	305.1	744.69
217.2	745.41	305.2	746.24
217.3	747.10	305.3	747.79
217.4	748.80	305.4	749.36
217.5	750.50	305.5	750.91
217.6	752.20	305.6	752.47
217.8	753.90	305.7	754.03
217.9	755.31	305.8	755.60
218.0	759.02	305.9	757.17
218.1	760.74	306.0	758.74
218.2	762.46	306.1	760.32
218.3	764.18	306.2	761.90
218.4	765.91	306.3	763.48
218.5	767.63	306.4	765.06

Apparatus for Vapor Tensions.

Under the atmospheric pressure the above substances can be used for fixing the scales of thermometers or for correcting them in any kind of glass apparatus, and when a thermometer is to be used for ordinary distillations the corrections can be most conveniently made by boiling in the same vessel some substance of known boiling point falling nearly at the same temperature; and if the scale cannot be entirely heated, the same number of degrees may be left outside in the two cases to be compared. With proper precautions a series of corrections can be thus established with an error of less than 0.5°; but the temperatures that are read off on the thermometers under these circumstances are not usually the true ones, and the corrections must be based upon the known boiling points of the standard substances, which have been determined with special care. Some directions regarding the use of corrected thermometers with a limited scale are given further on under the heading Distillation, but a greater accuracy has been aimed at with the standard apparatus destined for the manufacture or the exact correction of thermometers. The chief difficulty is to avoid superheating the lower strata of vapor, when a column high enough to envelop the scale of the thermometer is heated. If, for instance, benzophenone is boiled in a large glass vessel, with a neck at least 5 cm. wide, it requires a very powerful heat to maintain a column of vapor 30–40 cm. high, and an ordinary long thermometer is found to vary 2 to 3 tenths of a degree according as it is raised or lowered a few centimeters in the vapor.

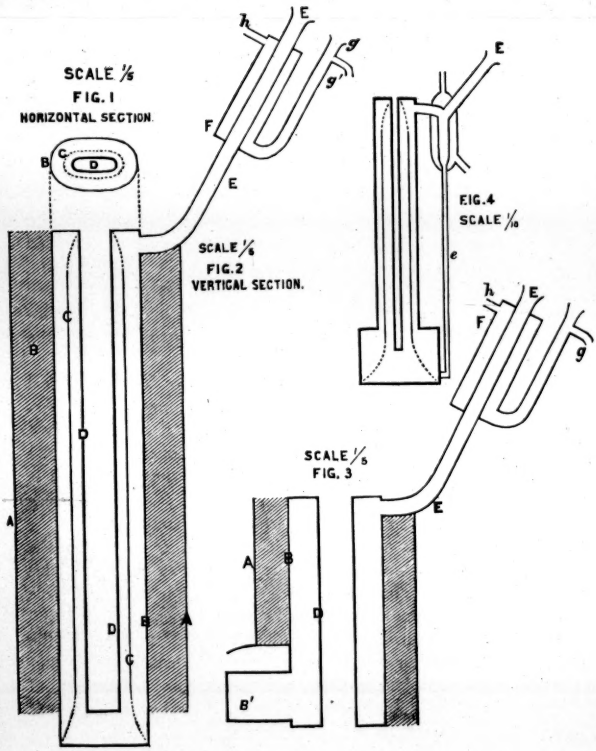
Considerably better results are obtained by surrounding the neck of the flask with a non-conducting jacket of plaster or mineral wool, and following in the direction thus indicated, various forms of metallic apparatus were constructed, in which a sensitive thermometer with a short scale showed the same temperature to within less than one-tenth degree when placed at any height above the boiling liquid.

Figures 1 and 2 represent a copper apparatus specially adapted to the graduation of thermometers. The metal is 2 mm. thick and will bear a pressure of two atmospheres. All the parts are brazed. The space between the true apparatus *B* and an outer cylinder *A* made of stove-pipe is 3½ cm. It is filled with mineral wool to prevent radiation. *B* is 8 cm. largest diameter and 47½

long. The section Fig. 1 shows its elliptical form, and the smaller diameter is 5½ cm. *C* represents an inner tube of thin copper intended to protect the vapors from condensation. It is pierced with holes as shown by the dotted portions near the bottom and the top. The vapors rise principally between this tube and *D*, and the condensed liquid runs down the sides of *B*. *D* represents a flattened tube 3 cm. by ½ cm. in section and 43 cm. long. It contains 5 or 6 thermometers, which can be conveniently observed together by means of a telescope. When the thermometers are nearly of the same size they may all be held at the requisite height by the slight pressure of a single spring clamp, or they may be grasped by a series of watch-spring clamps or simply suspended from threads. An easy adjustment of the height is important. The vapors are condensed in the tube *E*, and the condenser is of a peculiar form to prevent the stoppage of the tube by the solidification of crystalline substances. Water is allowed to flow constantly into *g*, and out drop by drop at *g'*, and the water consequently remains always at the level of *g'* in the condenser. The water is soon heated to boiling, the steam escapes at *h*, and the vapors of naphthalene and other substances are condensed at 100° instead of at the ordinary temperature, and flow back as liquids. In an ordinary operation it is not even necessary to renew the water, and it is only when the heating is long-continued that a flow of water becomes necessary. For substances which like benzoic acid melt higher than 100°, the water may be replaced by amylic alcohol or by some other convenient liquid, and a lead tube (not shown in the figure) soldered upon *h* can be so arranged as to return the amylic vapors in the form of liquid to the condenser at *g*.

The apparatus of Figs. 1 and 2 is long enough to heat any ordinary thermometer, but when a great subdivision of the scale makes it of unusual length, the protruding portion of the stem is heated to the same temperature by the cylinder (Fig. 3), which is put upon the top of the first, and contains the same standard substance. The non-conducting jacket is so arranged as to allow the flame to play around *B*, and this part of the cylinder projects enough to allow a lamp to be placed under it. Any number of such cylinders may be superposed, so that there is no limit to the length of a thermometer which may be heated to a fixed temperature without danger of superheating the vapors.

Several questions regarding the accuracy of this method of fixing temperatures required to be studied experimentally.


SCALE 1/5
FIG. 1
HORIZONTAL SECTION.
SCALE 1/5
FIG. 2
VERTICAL SECTION.
FIG. 4
SCALE 1/10
SCALE 1/5
FIG. 3
A
B
C
D
E
F
g
g'
h
e
B'

The temperature was found to be exactly the same whether the interior tube D was used as an air-bath or was filled with high-boiling paraffin, and the use of oil or paraffin was rejected because it has many inconveniences. The tube D can be made cylindrical and of much larger dimensions to fit it for air thermometer work, without making any difference in the temperature, when the mouth is well stopped with asbestos.

It was thought possible that the condensed liquid from E flowing back along the sides of D might lower the temperature, and comparative experiments were made with the apparatus described and with that represented on a smaller scale (Fig. 4), in which the vapors are so condensed as to be returned by the small tube E to the bottom of the apparatus. The results were identical in each case.

Other experiments were made by enlarging the bottom of the cylinder and by varying the quantity of the liquid, and it was found that such variations made no difference in the temperature, provided radiation of heat was well guarded against. The simplest form, Figs. 1 and 2, was therefore chosen, and it is believed that it is well adapted to obtaining the true boiling point of a high-boiling substance, as Rudberg's (Regnault's) apparatus is to measuring the boiling point of water.

A smaller apparatus, in which the interior tube D is cylindrical and only 5 mm. in diameter, is used for examining a single thermometer, and it can be used more quickly since it requires only 6 to 8 minutes for the temperature to become stationary. With the larger apparatus a longer time is required, and the error which is most likely to occur on working with it arises from not waiting patiently until the mercury column has become stationary.

The thermometers are plunged in the tube D so that at the moment of reading only about 1° appears above the top. This requires a certain adjustment, which can be made after they have been heated about ten minutes; and since this operation may bring cool parts of the stem in contact with the tube D, and change the temperature of the air-bath, 8–10 minutes must usually elapse after the final adjustment before the temperature becomes constant and before the final reading should take place. For this cause there is even a certain advantage in replacing the single tube D by a number of smaller ones, each containing a single thermometer.

The liquid must be made to boil constantly, so that the condenser is heated with about equal rapidity in all determinations, a point which there is no difficulty in appreciating.

All these forms of apparatus can easily be connected at *E* with a reservoir of about 20 litres capacity, filled with air at any pressure, and no difficulty was found in boiling naphthalene and benzophenone under pressures varying from 100 to 1500 mm., so that any temperature within the ordinary thermometric scale can be determined, and the apparatus can thus be used for correcting or for graduating the whole scale.

The examination of different points in the scale of a thermometer by means of such an apparatus may replace advantageously all the corrections arising from errors of graduation, calibration, and the departure from the air thermometer scale. The operation is more accurate and infinitely less tedious than the usual ones for temperatures higher than 100°.

Corrections for Thermometers with a Limited Scale.

If the points 100° and 218° or 218° and 306° are so fixed on the scale of the mercury thermometer that they exactly agree with the measures that would be obtained by a hydrogen thermometer, a different table of corrections must be used to bring determinations made on intermediate points of the scale in agreement with the hydrogen thermometer, and the following tables give these corrections for each case of a limited scale. The 1st horizontal column gives the temperatures, and the 2d the corrections that are to be applied (taking notice of the signs + or —) to transform degrees on the mercury thermometer into two measures of temperature as determined by the hydrogen thermometer.

Table No. 1—*Scale* 100°–218°.

Temp. .	100°	110°	120°	130°	140°	150°	160°	170°
Correc. .	0.00	+0.01	+0.02	+0.07	+0.13	+0.21	+0.28	+0.29

Temp. .	180°	190°	200°	210°	218°	220°	230°
Correc. .	+0.28	+0.25	+0.19	+0.09	+0.00	—0.02	—0.12

Table No. 2—*Scale* 218°–306°.

Temp. .	210°	218°	220°	230°	240°	250°	260°
Correc. .	—0.06	0.00	+0.02	+0.09	+0.15	+0.21	+0.26

Temp. .	270°	280°	290°	300°	306°	310°	320°
Correc. .	+0.33	+0.37	+0.30	+0.15	0.00	—0.06	—0.31

As it is supposed that the thermometers intended for this use have been subjected to a preliminary treatment at 355°, no great permanent displacement of the zero point can take place in subsequent experiments, and with a limited scale the extent of the temporary depressions and elevations of the zero point is not large; however, in accurate work this point should always be observed after a measure of temperature, and a correction made for its displacement, and the above tables are adapted to results thus corrected.

In these thermometers the value of the degree is derived from a verification of the terminal points of the scale by means of boiling water, naphthalene or benzophenone, and if these points are inexact on the mercury thermometer, all the measures must be multiplied by the fractions representing the true value of the degree. The terminal points on the scales of these thermometers are to be determined for graduation or for verification by observing first the higher temperature, and it is well to heat several hours at this temperature to avoid any considerable displacement of the zero during graduation. The lower point is then determined as rapidly as possible.

It may be noticed that the corrections are very small compared with those which are applied to the ordinary scale running from zero to 360°, and they are almost identical for all thermometers. If smaller limits are taken for the scale, and points are fixed 50° apart in accordance with a gas thermometer, the corrections are so small for the intermediate points that no series of determinations which have been thus far made with the air thermometer are accurate enough to determine them with certainty; and the agreement between the scales of different instruments, which becomes closer as the points are taken nearer together, may be considered as almost perfect when the intervals are only 50°, and sufficiently exact for all common uses when the intervals are about 100°.

The Evaporation of the Mercury in the Thermometer.[1]

When the thermometer has been made entirely vacuous of air, a rapid evaporation of mercury may be observed even at 100°, when

[1] This phenomenon has been noticed by every one who has paid attention to thermometric measures, and has even been mentioned in some publications; but the errors which it may entail seem sometimes to have been neglected, and it will be seen by what has been said above that the evaporation of mercury might be a permanent cause of error in the results obtained with thermometers whose stem is left open to the air when they are heated to high temperatures.

the whole of the stem is heated in steam. If the necessary precautions are taken to set aside all other influences which would change the height of the mercury column, it may be observed to fall from minute to minute when it is watched with a good micrometric telescope; and after a quarter of an hour a variation of 0.01° or 0.02° is noticed. At high temperatures the evaporation of mercury is much more rapid, and is frequently a source of great inconvenience, disturbing the observations and dividing the mercury column by the condensation in the cooler parts of the stem. The evaporation is quite appreciable in experiments which last several days, even when the mercury is only heated 10° or 20° higher than the temperature of the air. When air is left in the stem of the thermometer the evaporation of the mercury is much retarded; but even in this case, when the stem of the thermometer is heated to 250°, a loss of mercury equivalent to several tenths of a degree may take place within half an hour. If the zero point is observed after each measure of temperature as has been recommended, the apparent sinking of temperature caused by the evaporation of the mercury does not give rise to an error.

The Purity of the Mercury in a Thermometer.

If the mercury which is used to fill a thermometer has not been well purified, or if it has not been boiled long enough in the thermometer to free the bulb and stem from air adhering to their sides, the mercury column is divided by air bubbles after long use at high temperatures. Even if the air bubble is driven into the upper reservoir, another one frequently forms in the same place, and such a thermometer becomes entirely useless. Even when it is intended to leave air in the upper reservoir, the boiling ought to be carried out as in a thermometer which is to be left vacuous, and it is advantageous to boil the mercury while the thermometer is connected with a Sprengel's pump. It seems probable, from the observations that have been made with thermometers and barometers, that when a layer of air or moisture has been left between the mercury and the glass it may serve as a channel by which further quantities of air or moisture may penetrate, and inconveniences are noticed with such instruments which certainly do not occur with those which are made with great care.

According as thermometers are well or ill made in these respects every degree of excellence may be noticed between those which

will not bear a single heating, even of a few minutes at 200°, without having the column broken, and those thermometers which are so well made that they may be heated for many days at 355° without showing the slightest air bubble in the bulb. This last was the case with four out of eight thermometers heated for eleven days and nights at 355°.

The preliminary treatment of thermometers at high temperatures, which has been frequently referred to, brings out these defects in the manufacture, and those instruments which will not bear the test must be rejected.

In connection with this subject may be mentioned a paper by Mr. Wiebe.[1] This author has repeated and confirmed my experiments upon the diminution of the coefficient of expansion of glass which accompanies a permanent contraction of the bulb of a thermometer, and he has published a series of interesting observations on the relation between the two phenomena which are in accordance with the principal results of my experiments. On the other hand, he considers that the permanent elevation of the zero point (in other words, the contraction of the bulb) cannot be considered as principally due to the causes which I have assigned. This opinion is partly founded upon Mr. Wiebe's incorrect determinations of zero point depressions. Those published by him for the temperature 370° are probably less than one-third of the true value; and he appears also to have been misled by a theory which it will be interesting to examine. Mr. Wiebe supposes that a gas is disengaged from the glass on heating, and that a portion of the contraction of the bulb is due to this cause. He cites the experiments of Dumas, Lockyer, Miller, who have found that several metals, as well as phosphorus, give off a gas when they are strongly heated *in vacuo*.

It might be objected that these experiments would be little conclusive if it were true that glass and porcelain were like the metals in this respect, because these substances formed the material of the apparatus which was used. But let us suppose that a contraction may really result from the disengagement of a gas which fills the intermolecular spaces of glass; we may calculate the probable extent of the contraction by taking the necessary data from well-known experiments with palladium. This is the only metal with which the phenomenon has been studied with reference to the

[1] Metronomische Beiträge, No. 3.

contraction of a solid body produced by a loss of gaseous material. It may be added, however, that the results would be six or eight times more favorable to the hypothesis of Mr. Wiebe if they were based upon the solution of hydrochloric acid or of ammonia in water.

Mr. Wiebe has given no measures of the quantity of gas which was observed on heating and which separated the mercury column in his thermometers. The volume of the gas can be measured when the mercury is not made to boil, and I will take the largest quantity which I have observed as a basis for a calculation. During an elevation of the zero point equal to 17°, a bubble of gas was formed on the side of the bulb; this was eventually brought into the stem, where it separated the column of mercury and filled a space equivalent to 1.35°. The contraction of the bulb was equivalent to 0.0026 part of the total volume occupied by the mercury. This latter volume may be taken as unity, and the quantity of gas disengaged was equivalent to 0.00021 part. The volume of the glass of the bulb relatively to the mercury may be taken at 0.2, which is a usual proportion in thermometers whose bulbs and mercury are weighed for specific heat determination. (The relative volume of the glass in my thermometer was really larger.) We will suppose that only half the gas is emitted into the interior of the thermometer. We will suppose that the contraction of palladium is proportional to the quantity of hydrogen disengaged. (It is really smaller when the volume of hydrogen is small.)

It would result that a diminution of volume from 1.0026 to 1.0000 would be accompanied by an evolution of more than 15 volumes of gas. Divide this number by 2 to express that only the half of the gas disengaged by the glass of the bulb appeared in the interior of the thermometer, and by 5 because the volume of the glass is supposed to be only equal to one-fifth that of the mercury, and we find that 1.5 volume of gas should be given off if the contraction were due only to this cause.

It may be concluded that the quantity of gas disengaged in the experiment most favorable to the theory of Mr. Wiebe was 7000 times smaller than the quantity required by the calculations founded on the above hypotheses, or that $\frac{1}{7000}$ of the effect is attributable to a disengagement of gas. This discrepancy becomes still greater when it is remembered that the bubble measured was not under atmospheric pressure, as assumed in the calculation, but

under a much smaller pressure, and in the experiments where no gas was disengaged no part of the phenomenon is accounted for by Mr. Wiebe's hypothesis.

It may also be observed that, did the glass of a thermometer evolve a gas in sufficient quantity to account for a notable contraction of the bulb, the pressure of this gas would be quite appreciable, even in thermometers which have an upper reservoir, while in those which have none and are particularly intended for use at high temperatures, the pressure might amount to several hundred atmospheres at a moment when the stem is filled with mercury, leaving a free space of only some 50°.

I have taken the only data known regarding a solid; but, as has already been remarked, the numbers would be more favorable to the views of Mr. Wiebe if the calculation were based upon the absorption of hydrochloric acid or ammonia by water, and the discrepancy between the facts and the theory would be reduced from 7000 to 700 if the gas were supposed to be oxygen with the same density, when condensed to a liquid, as water.[1] But these numbers, ranging in my experiments from 700 to infinity, indicate too strong probabilities against the hypothesis in question to make it worth further consideration.

This subject has been treated under the heading of "Purity of the mercury in a thermometer," because it is believed that the vexatious appearance of bubbles is usually due to want of care in the manufacture of thermometers. It may be added that at temperatures so high as 370°, particularly when the mercury boils, a rapid movement of the column may imprison air from the reservoir, and that wherever a bubble has once formed it is apt to reappear. Perhaps, as has been said, the *moistening* of the glass by a gas may extend to the formation of a permanent canal along the stem, between the mercury and the glass, through which gas passes, particularly when the mercury is in rapid movement. The following experiment has some bearing on the subject: A clean capillary tube, plunged deep under the surface of mercury, serves to suck up an unbroken column of mercury; but even a short exposure of the tube to the air of a laboratory coats it with a film of chloride of ammonium, and then when the mercury is made to flow up through it, bubbles of air are drawn down between the

[1] The theory of M. Dumas and the experiments of M. Raoul Pictet indicate the density of liquified oxygen is about 1.

mercury and the outside of the capillary tube, and a broken column appears in the tube. Thus, a thermometer which has not been sufficiently cleaned is particularly liable to the defect of the formation of bubbles.

The Influence of Pressure upon a Thermometer.

The most complete series of experiments upon this subject has been made by Mr. Mills, who has studied the relation between the rise of the mercury in the stem and the pressure exercised upon the bulb of the thermometer. In one series of his experiments the rise was 0.106° for every atmosphere of pressure up to 133 atmospheres.

According to Mr. Mills, an excess of pressure of 1 atmosphere causes a rise of about 0.2°; but this factor must be determined for every thermometer separately. It appears to be in inverse ratio with the thickness of the glass, but depends also upon the form of the bulb; and it is evident that a fault in the symmetry of the bulb might considerably increase the compressibility of a thermometer.

It is apparent from the above figures that the variations in the barometric pressure may be neglected from this point of view; but it is frequently necessary to take into account the differences of pressure, which depend upon whether the thermometer is placed horizontally or vertically, and, in a long thermometer, the variations of the zero, or better, of the boiling point, which ensue upon a change of position, may be used to calculate approximately the coefficient of compressibility of a thermometer.

Variations of this kind must be allowed for in distillations *in vacuo*, and in all similar operations where the thermometer is subjected to a diminished or increased pressure; but it is frequently preferable to avoid such corrections by placing the thermometer in a very thin tube, closed at its lower extremity, and communicating with the air at its upper end. For another reason it is frequently convenient to enclose the thermometer in an extremely thin glass tube, like those which are used for making the stems of areometers, in order to prevent the black coloring matter (usually a mixture of wax and lampblack) from being dissolved away from the division marks on the scale. If the tube is thin and of nearly the same diameter as the thermometer, and a little mercury is put in the bottom to cover the bulb, the sensitiveness of the thermometer is very little diminished, and thermometers so arranged respond

more quickly to change of temperature than those of the German model, which have a portion of the bulb covered by a great thickness of glass at the point where an exterior tube containing the scale is soldered to the bulb.

Distillation.

When the substance is pure, and when the above precautions regarding the use of thermometers have been observed, errors in the determination of the boiling point arise most frequently from too hasty operations. The mercury in the bulb takes the temperature of the vapors almost immediately, but the same is not true of the mercury column in the stem, which has to be heated through a great thickness of glass, and, what is of still more consequence during this process, the liquid which is at first condensed very rapidly on the upper part of the stem runs down and cools the bulb. Even when all the mercury column is surrounded by the vapor of the boiling substance, and the apparatus is in every way well arranged to guard against loss of heat, 5 to 10 minutes are required for the temperature to become constant, and during this period the apparatus should be held in such a position that the liquid in the condensing tube may flow back, and from time to time during the distillation it is well to heat for a few moments without allowing any substance to pass over into the recipient in order to see if a constant temperature has been attained.

With substances boiling at a very high temperature it is somewhat difficult to obtain a column of vapors sufficiently long to heat the stem of the thermometer without overheating the vapors near the bulb. And where the metallic apparatus before described cannot be used, the difficulty of dealing with high-boiling substances is greatly lessened by surrounding the apparatus with a jacket at least 2 cm. in thickness of plaster of Paris or asbestos cloth, leaving only a portion of the bottom of the boiling vessel exposed to the flame. This portion can be usually entirely covered with the substance which is to be distilled, so that the flame does not at any point come in contact with the part of the apparatus containing the vapors. When plaster of Paris is used, such an apparatus must be maintained 2 or 3 hours at high temperatures before the water is evaporated out of the plaster, and in fact the moment when the apparatus is ready for use can be observed by the very much smaller flame required to maintain active ebullition. When the

glass apparatus has a disengagement tube soldered into its neck the plaster must not be allowed to set at the joint, it should be scraped away from the part while soft, although the protecting jacket should be carried about 2 cm. higher round the neck. Where a substance is known to have the same boiling point at the beginning and at the end of a distillation, or when the quantity of the substance is too small to admit of a fractional distillation, the boiling point may be conveniently tested in an ordinary test tube surrounded by a plaster cylinder; for instance, if sulphur is made to boil in this way, the plaster becomes dry after 2 or 3 hours, and then the condensation takes place almost entirely on the part of the naked tube immediately above the plaster cylinder. A cylinder so prepared and dried may be slipped over other test tubes and used for all boiling point determinations. Experiments with such an apparatus filled with mercury or sulphur, and using an air thermometer, have shown that the boiling point determinations are reliable to within 0.2°.

Melting-point Determinations.

When a sufficient quantity of substance can be disposed of, it is best to introduce a small and sensitive thermometer into the liquid, and to observe all the changes of temperature during the complete solidification.

It is usual to take melting points of small quantity of matter in a capillary tube attached to a thermometer, and both are heated in a sulphuric acid bath or in a paraffin bath[1] for temperatures higher than 300°. It is only necessary to remark upon a modification of this process in which the apparatus contains an interior tube, which is used as an air bath, surrounded by sulphuric acid. This form of apparatus was devised to prevent the sulphuric acid vapors from escaping into the air, and to prevent the acid from attracting moisture. These ends could be obtained more simply otherwise, and the apparatus has a grave defect. It is only necessary to heat a large and a small thermometer together in an air bath at changing temperatures to see that one is constantly behind the other in its indications, and it is quite certain that a small mass of substance in a capillary tube would be usually heated more quickly than a thermometer placed beside it, when they are both heated in an air bath at rising temperatures. It is therefore indis-

[1] It is not difficult to find English paraffin candles, which are so well purified that after distilling a small portion of the more volatile hydrocarbons it enters into active boiling above 370°.

pensable in melting point determinations to heat the thermometer and the capillary tube together in a liquid, and not in any form of air bath. The numerous forms of apparatus proposed for observing points of fusion have often been applied with good results to special cases, but the ordinary method is on the whole the most convenient, and few substances are known of sufficient purity to demand a process of greater accuracy. The method which is most nearly perfect is that which is always used with melting ice, and it would be interesting to heat such other solids as can be obtained pure in sufficient quantities in an air bath at a temperature somewhat higher than their melting points and to observe the degree of constancy attained by a thermometer properly surrounded by the melting solid.

ON THE ACTION OF ALDEHYDES ON PHENOLS.

I.

By Arthur Michael.

The investigation of the action of aldehydes on phenols was begun by A. Baeyer,[1] shortly after the discovery of the phthaleïns. It was found that by heating benzoic aldehyde with pyrogallol a resinous compound of the composition $C_{26}H_{22}O_7$ was formed. Concentrated sulphuric acid on a mixture of benzoic aldehyde and resorcin gave a reddish resin, and amorphous compounds are formed in the action of sulphuric acid on mixtures of ethylaldehyde or chloral and phenol or pyrogallol. In the following paper[2] Baeyer used a large quantity of concentrated chlorhydric acid to obtain the resin $C_{26}H_{22}O_7$ from benzoic aldehyde and pyrogallol. When the mixture was heated, besides the reddish resin, a crystalline compound was obtained. This compound, which is isomeric with the resin, was more easily obtained by adding the acid gradually to a boiling alcoholic solution of benzoic aldehyde and pyrogallol. Salicylaldehyde and pyrogallol gave, under similar conditions, the compound $C_{26}H_{22}O_9$; while from benzoic aldehyde and naphthol the compound $C_{34}H_{26}O_3$ was obtained. These compounds are formed from an

[1] Berichte der deutschen chemischen Gesellschaft, **5**, 25. [2] *Ibid.* **5**, 280.

equal number of molecules of aldehyde and phenol by the loss of an equal number of molecules of water; $2C_6H_5—CHO + 2C_6H_3(OH)_3 = C_{26}H_{22}O_7 + 2H_2O$. In a third communication[1] it was stated that concentrated chlorhydric acid acting on mixtures of methylal and phenol or resorcin gave resins, while pyrogallol and gallic acid yielded a small amount of crystalline products. None of these products have been since examined, but a number of investigations on the action of aldehydes on phenols, under somewhat different conditions, came from Baeyer's laboratory in the following years. Jaeger[2] obtained, by the action of a large quantity of concentrated sulphuric acid on a mixture of chloral and thymol, the compound $CCl_3—CH(C_{10}H_{13}OH)_2$. Ter Meer,[3] in a similar manner from methylal and methylphenyloxide, the compound $CH_3=(C_6H_4OCH_3)_2$; and from chloral and phenol, $CCl_3—CH=(C_6H_4OH)_2$ was obtained. Later, by using tin tetrachloride instead of sulphuric acid, a condensation product of ethylaldehyde and phenol was obtained. Fabinyi[4] from ethylparaldehyde and phenol obtained a small yield of ethylidenediphenol, $CH_3—CH(C_6H_4OH)_2$; and Steiner,[5] from chloral and thymol, trichlorethylidenedithymol. Very recently, C. Etti,[6] in the Vienna University laboratory, by the action of a large quantity of concentrated chlorhydric acid (50 parts to one part of aldehyde), believes he has obtained from vanillin and pyrogallol the crystalline compound $C_{20}H_{18}O_8$; from vanillin and phloroglucin an isomeride of that compound. I shall return to Etti's investigation towards the end of this paper. The one result common to all these investigations is the formation of complicated substances from aldehydes and phenols by linking of carbon to carbon, and elimination of water. Beyond this there is considerable discrepancy. Baeyer obtained by the action of equal molecules of benzoic or salicylic aldehyde and pyrogallol, compounds formed by the elimination of an equal number of molecules of water; while Etti obtained from a different aromatic aldehyde, vanillin, and pyrogallol, under the same conditions, a compound derived from one molecule of aldehyde and two molecules of the phenol with a loss of one molecule of water. The last reaction is the type of that occurring between methyl or ethylaldehyde and phenols, when sulphuric acid, or tin tetrachloride, is used as the dehydrating agent. Are these differences due to inherent proper-

[1] Berichte der deutschen chemischen Gesellschaft, **5**, 1094. [2] *Ibid.* **7**, 1197.
[3] *Ibid.* **7**, 1200. [4] *Ibid.* **11**, 283. [5] *Ibid.* **11**, 287. [6] Monatshefte für Chemie, **3**, 637.

ties of the aldehydes, or to the somewhat different conditions of the experiments? In all these experiments it is supposed that the presence of a strong dehydrating agent is a necessary condition. What relation exists between the resin obtained from benzoic aldehyde and pyrogallol, and the crystalline compound obtained under slightly different conditions? In regard to the constitution of the compounds that have been obtained from aromatic aldehydes and phenols, absolutely nothing is known. Has this resin-formation from aldehydes and phenols a connection with the formation of resins in the vegetable world? In other words, have the contents of the cells the property of forming these resins? and do they resemble in their properties those found in nature? These are some of the questions that led to a reinvestigation of the action of aldehydes on phenols.

In the present paper I shall confine myself to the description of the experiments that have been made in the study of the action of benzoic aldehyde on resorcin. The investigation is coupled with such experimental difficulties that, although considerable time has been spent on it, hardly more than a foothold for future service has been gained. The action of heat on a mixture of benzoic aldehyde and resorcin was first examined. In open vessels the mixture—resorcin dissolves in the aldehyde on heating—may be heated for days without a reaction ensuing. In closed tubes and heated to 200° a resin was formed, which was not examined.

In striking contrast is the readiness with which benzoic aldehyde and resorcin react in presence of acids. Baeyer had already found that concentrated sulphuric acid poured on a mixture of these substances converted them into a red resin. A few experiments sufficed to show that it is advantageous to moderate the violent action by dissolving the aldehyde and phenol in alcohol, and that the function the acid plays in the reaction has been completely misunderstood. If to a solution of one gram of benzoic aldehyde and one gram of resorcin in three grams of absolute alcohol, a drop of concentrated chlorhydric, or sulphuric acid, is added, it will be noticed that as soon as the acid comes in contact with the solution a resinous substance is formed, which immediately dissolves in the alcoholic solution. A rise of temperature takes place, under the above conditions, to 55–60° C., and the solution soon becomes quite thick; at the same time a deposit of a crystalline substance takes place. If the filtered alcoholic solution, after it has cooled, is

poured into a large quantity of water, a white amorphous compound settles, which is the first product of the action of the acids on benzoic aldehyde and resorcin. It is easy to prove that the formation of this product is entirely independent of the affinity of the acid for water. A trace of chlorhydric acid, less than $\frac{1}{8}$ of a drop, causes the formation of the same resin, the only difference being that the reaction proceeds somewhat more slowly, and a natural consequence thereof that the solution becomes less warm. Instead of three parts of absolute alcohol, twenty parts may be taken, without changing in the least the final result; or a drop of chlorhydric acid may be dissolved in a considerable amount of alcohol, and then added, with the same result. Nor is absolute alcohol necessary, dilute alcohol will serve the same purpose; only, if too dilute, the resin will separate from the solution as it is formed. Still more conclusive were the experiments proving the resin-formation in the presence of water. If to equal parts of the aldehyde and resorcin and twenty parts of water a drop of chlorhydric acid is added, and the mixture heated to boiling, the aldehyde gradually unites with the resorcin, and is completely converted into the resin. A drop of chlorhydric acid is sufficient to induce the reaction between a considerable quantity of aldehyde and resorcin. In one experiment twenty grams of these substances were completely converted into the resin by a single drop of acid.

To obtain the resin suitable for analysis, a drop of chlorhydric acid was added to a solution of equal parts of aldehyde and resorcin in three parts of alcohol, the solution allowed to cool, filtered, and the filtrate poured into water. The precipitated white resin was extracted several times with a large quantity of cold water, dissolved again in a small amount of alcohol, and reprecipitated by pouring into water. All attempts to obtain this compound in a crystalline form were without success. The white substance, when it contained considerable water, remained unchanged on contact with the air; but it could not be obtained free of water, as it became dark on standing in the air three or four hours. An attempt to dry it in a partial vacuum was also without result. In order to free the substance of water, it is necessary to heat it in an atmosphere of carbon dioxide or hydrogen. The pulverised resin, after being well pressed between filter paper, in a platinum boat, was brought into a tube, one end of which is connected with a series of drying tubes, and these with a Kipp's carbon dioxide generator,

and the other end with a calcium chloride tube. The tube is enclosed in a glass jacket, through which steam can be passed. Even after passing a slow current of dried carbon dioxide for forty hours over the resin in the cold, it was found that a decided loss in weight occurred in the next four hours. Moreover, notwithstanding the precautions taken to prevent the ingress of air into the apparatus, the substance had taken a decided reddish tinge. Heated to 100° in a current of carbon dioxide, the resin melted, a property which is due to the presence of water, and gave off, comparatively, a very considerable amount of water. It is probable that it either contained water in the form of so-called water of crystallisation, or the action of heat caused a condensation. The reddish resin, which when dry did not melt at 100°, and powdered had but a slight reddish color, gave the following numbers on analysis:

0.1928 gram of substance gave 0.5577 gram of CO_2 and .0977 gram of water.

0.2285 gram of substance gave 0.6601 gram of CO_2 and 0.1135 gram of water.

Theory for $C_{28}H_{20}O_4$.		Found.	
C	78.69	78.83	78.78
H	5.05	5.62	5.51

The white resin, before drying at 100°, is insoluble in boiling water, but melts under it to a reddish mass. It is very soluble in alcohol, benzene, ether and glacial acetic acid. On exposure to the air it gradually takes up oxygen, and is converted into a dark brown substance; a decomposition which takes place very rapidly when the resin is heated. It dissolves very readily in alkalies, to form colorless solutions, which are extremely sensitive to the action of oxygen. The solutions, exposed to the air for several minutes, take a dark brown color.

The properties of the dried resin in reference to solubility and behavior towards alkalies do not differ from the above. It melts, however, only at a high temperature—above 330°—under complete decomposition, and remains solid under boiling water. These differences are sufficient to show that the resin has undergone a decomposition more than the loss of uncombined water. The analysis and properties of the resin, when dried until constant weight in a partial vacuum, show this more conclusively. The red, dried substance gave off water on heating at 100°. No further impor-

tance is to be attached to the following analysis than as showing that the substance dried in a vacuum contained water other than mechanically mixed, since the red color of the substance indicated a partial oxidation.

0.2160 gram of substance gave .5491 gram of CO_2 and .1043 gram of H_2O.

Theory for $C_{26}H_{20}O_4$, $3H_2O$.	Found.
C 69.34	69.33
H 5.77	5.32[1]

To obtain the acetyl derivative, the white resin was well pressed out between filter paper, dissolved in five times its weight of acetic anhydride, and an equal weight of fused sodium acetate added. The mixture was heated to boiling for an hour, and then poured in a large amount of water. The precipitate was dissolved in alcohol, filtered, and reprecipitated by addition of water. An analysis gave the following numbers:

0.2150 gram of substance, dried at 100°, gave .5681 gram of CO_2 and .1062 gram of H_2O.

Theory for $C_{26}H_{16}O_4(OCCH_3)_4$.	Found.
C 72.31	72.16
H 5.17	5.48

The white, amorphous acetyl derivative is somewhat less soluble in alcohol and benzene than the mother-substance. It is insoluble in alkalies in the cold. When heated with them it gradually dissolves, the solution becoming dark brown.

The crystals that separate from the alcoholic solution of benzoic aldehyde and resorcin on addition of chlorhydric acid, are formed by action of the acid on the white resin, the first product of the reaction. This may be easily proven by adding a drop of the acid to a clear solution of the resin in alcohol. The temperature of the solution does not change, but soon the formation of a crystalline deposit will be noticed. The amount of the crystalline compound formed is dependent on the quantity of acid added; not, however, on the concentration of the acid. If to the filtrate of the aldehyde-resorcin mixture, after the formation of precipitate caused by the addition of a drop of acid, a second drop is added, a further pre-

[1]The hydrogen estimation shows that the substance was partially oxidised. The constitution of the white resin is probably $C_{26}H_{20}O_4$, $2H_2O$, or $C_{13}H_{12}O_3$. I shall endeavor to obtain it in form suitable for analysis.

cipitate is deposited; the amount formed being the same whether the acid is concentrated or previously diluted with alcohol.

The crystals consist of two substances, one crystallising in needles, and the other in square plates. A convenient method of preparing these substances is based on the action of acids on a solution of the resin in an aqueous solution of resorcin. A mixture of five parts of benzoic aldehyde, ten parts of resorcin, and twenty parts of water, on heating, formed a clear solution. To the hot solution three or four cc. of water containing several drops of concentrated chlorhydric acid were added, and the solution heated on a hot water-bath as long as a precipitate was deposited. The slight reddish precipitate was separated by filtration, and the filtrate, again treated with acid and heated, yielded a further quantity of the crystalline products, which had a decided yellow color. That the first product formed in this method of preparation is the resin was shown by extracting the solution, after heating it for a moment, with ether. The extract contained resorcin and the white resin. The crystalline deposits were extracted several times with a large amount of boiling alcohol, filtered while hot, and the filtrate, allowed to stand, deposited square plates. For analysis they were recrystallised several times from alcohol. The analyses of the substance, dried at 100° in a current of carbon dioxide, gave the following numbers:

0.2038 gram of substance gave 0.5852 gram of CO_2 and 0.0957 gram of H_2O.

0.2082 gram of substance gave 0.5968 gram of CO_2 and 0.1008 gram of H_2O.

	Theory for $C_{26}H_{20}O_4$.	Found.	
C	78.69	78.32	78.13
H	5.05	5.27	5.38

The substance does not decompose on exposure to the air.

0.4769 gram of air-dried substance lost 0.070 gram of H_2O when dried in CO_2 at 100°.

0.2450 gram of air-dried substance lost 0.0357 gram of H_2O when dried in CO_2 at 100°.

	Theory for $C_{26}H_{20}O_4$, $4H_2O$.	Found.	
H_2O	15.37	14.68	14.57

The hydrated compound separates from alcohol in colorless quadratic plates or prisms. It is moderately soluble in hot, very sparingly in cold alcohol; insoluble in water and ether. Alkalies

dissolve it readily in the cold, and the solution soon becomes dark on exposure to the air. The addition of acids to a freshly prepared alkaline solution precipitates the substance in an amorphous form. This precipitate retains its amorphous character on boiling with water or acids, but separates from a hot alcoholic solution on cooling in quadratic plates. It melts at a high temperature (above 330°) under decomposition. In a partial vacuum most of the water of crystallisation was given off (C—77.11, H—5.45), but the substance took a decided reddish color. Fused with caustic potash and a small quantity of water, at a low heat, until the addition of acid to a test did not cause a precipitate, the flux dissolved in water. Acidified, and then rendered slightly alkaline with sodium carbonate, it gave resorcin on extraction with ether. In the alkaline solution the presence of benzoic acid was proven.

Acetic anhydride does not dissolve the hydrated substance, even on boiling. A mixture of the substance, anhydride and fused sodium acetate, in proportion of equal parts of substance and salt and five parts of anhydride, gave on heating a clear solution, from which, on heating for several minutes, the acetyl compound completely separated. The crystals were separated by filtration, washed with alcohol and crystallised from boiling xylene. An analysis gave the following numbers:

0.2497 gram of substance, dried at 100°, gave 0.6621 gram of CO_2 and 0.1163 gram of H_2O.

	Theory for $C_{26}H_{16}O_4(C_2H_3O)_4$.	Found.
C	72.34	72.31
H	4.93	5.17

It is moderately soluble in boiling xylene, and separates on cooling in obliquely truncated, translucent prisms, which do not contain water of crystallisation. Insoluble in cold, but sparingly in hot alcohol. Cold alkalies do not dissolve it; when heated a gradual solution is effected, and the solution becomes dark colored. By heating anhydrous $C_{26}H_{20}O_4$ with acetic anhydride and sodium acetate an acetyl compound with the same physical properties was obtained.

To obtain a reduction product the crystalline compound $C_{26}H_{20}O_4$ was dissolved in hot alcohol, and zinc or tin and an alcoholic solution of chlorhydric acid added. From the hot solution white needles gradually separated. These were a compound of zinc or

tin chloride with the reduced compound. On decomposition the double compound gave a colored reduction product. In order to reduce in an alkaline solution it is necessary to exclude carefully the presence of oxygen. The alkaline solution in a small flask, through which a slow current of hydrogen gas passed, was treated with sodium amalgam, the liquid poured into dilute chlorhydric acid, avoiding, as much as possible, contact with the air. From the alcoholic solution of the amorphous precipitate crystals separated, which, dried at 100° in CO_2, on analysis gave the following result:

0.2357 gram of substance gave .6822 gram of CO_2 and .1188 gram of H_2O.

	Theory for $C_{26}H_{22}O_4$.	Found.
C	78.38	78.47
H	5.53	5.61

The substance is deposited from hot alcohol on cooling as quadratic prisms with end-faces. It appears to be somewhat more soluble in hot alcohol than the original substance, and also to oxidise more easily. The differences between the percentages of carbon and hydrogen of $C_{26}H_{22}O_4$ and of $C_{26}H_{20}O_4$ (C—78.69, H—5.05) are so small, and the properties of the described substances so much alike, that further proof of their non-identity is absolutely necessary.

The second substance formed in the action of acids on the white resin remained in the residue after extraction with alcohol, and was obtained pure by boiling out with a very large amount of alcohol. It is but slightly soluble in hot alcohol; one litre of alcohol dissolving about 0.15 gram of substance, which separated on cooling in white needles. The yield obtained of this substance is small.

The intensity of the action of benzoic aldehyde on resorcin depends largely on the acid used. While chlorhydric and sulphuric acids cause a rise of temperature to 55–60°, phosphoric acid induces a much slower reaction, and the temperature of the alcoholic solution only rises to 35–40°. Organic acids are still slower in causing the reaction. The following experiments were made with a solution of three parts of absolute alcohol, one part of resorcin and aldehyde.

Two drops glacial acetic acid were added. A rise of temperature did not take place. The crystalline substance began to form after several days standing, but the liquid still contained unchanged

benzoic aldehyde. After four days a considerable precipitate was deposited and the solution contained nothing but the white resin.

Three grams of glacial acetic acid. The reaction proceeded very slowly. A deposit began to be formed after standing two days, and the aldehyde and resorcin were not completely converted into the resin until the mixture had stood for a week.

Two drops formic acid. No rise in the temperature of the solution. The reaction was completed in two days. With lactic acid the result is similar.

One-half gram of oxalic acid. A precipitate was formed in 24 hours. It consisted principally of prisms, which appear to be more soluble in alcohol than the plates formed by chlorhydric acid.

Several preliminary experiments on the behavior of the aldehyde-resorcin mixture towards alkalies have been made. It is necessary to keep the solution as much as possible from the air, since the substances formed are rapidly oxidised in alkaline solutions. Caustic soda, potash and potassium carbonate, one-half gram of each, gave the same result. The solution took, after standing several hours, a brownish color. In 24 hours the substances were converted into the above-described, or a similar resin.

The action of aromatic aldehydes on phenols, in the presence of a small amount of acid, is to form an amorphous resin, but the facility with which this is formed depends on the nature of the phenol and aldehyde. In the cold a trace of chlorhydric acid caused no action between benzoic aldehyde and phenol in alcoholic solution, but several hours' heating sufficed to convert these substances quantitatively into a resin corresponding to the resorcin resin. The orcin mixture rose in temperature to 40–45°, while the pyrogallol mixture only reached 35–40° under the conditions that the resorcin mixture reached 55–60°. Similar results were obtained from salicylaldehyde and phenol. Although it is somewhat premature to discuss the constitution of the compounds formed, and the nature of the action of aldehydes on phenols, I wish to state briefly what appears, from our present knowledge, to be the most probable interpretation. Aromatic aldehydes and phenols are probably first converted, by carbon polymerisation, into oxy-carbinols by traces of mineral acids. Whether a trace or a large amount of acid is used it is probable that these compounds are the primary products of the reaction. The further action will depend on the presence of a dilute acid, or an excess of the phenol

and an acid with a strong affinity for water. With a dilute acid a condensation takes place; a result which is in accordance with the properties of the aromatic oxy-carbinols of undergoing a similar condensation when heated with traces of a mineral acid. Thus o-p-dioxybenzophenone[1] and dipara-dioxybenzophenones,[2] under these conditions, pass over into compounds which are probably derivatives of ethylene. In presence of a concentrated acid and a phenol, a different reaction may take place. The elements of water are extracted with the formation of a derivative of triphenylmethane. That the action of dehydrating agents on mixtures of secondary aromatic carbinols and aromatic hydrocarbons is to form triphenylmethane derivatives has been shown in a number of instances. It is possible that Etti, who used a very large proportion of fuming chlorhydric acid, has obtained compounds from vanillin and phenols which are derivatives of triphenylmethane; but the difficulty of obtaining this class of compounds in a condition suitable for analysis, unless proper precautions are taken to exclude the air, and the fact that Baeyer under the same conditions obtained compounds belonging to the ethylene group, show that further proofs than analyses are necessary before any confidence can be placed in his conclusions. Etti has apparently based his conclusions largely on a generalisation of Baeyer,[3] which that chemist evidently intended to apply only to the action of fatty aldehydes on phenols in presence of certain dehydrating agents. The experiments described in the following note make it probable that fatty aldehydes act on phenols, in the presence of traces of mineral acids, in much the same way as aromatic aldehydes do.[4]

The action of heat, or dilute acids, on the benzaldehyde-resorcin resin may be represented as follows:

$$2C_6H_5—CHOH—C_6H_3(OH)_2 = C_6H_5—\underset{\displaystyle C_6H_5—\overset{\displaystyle |}{C}—C_6H_3(OH)_2}{\overset{\displaystyle |}{C}}—C_6H_3(OH)_2 + 2H_2O.$$

This formula is in accordance with the existence of four hydroxyls and the compound taking up two hydrogen; but, as already stated, it cannot be considered other than as a suggestion.

[1] This Journal, **5**, 89.

[2] Annalen der Chemie, **202**, 132.

[3] Berichte der deutschen chemischen Gesellschaft, **12**, 645.

[4] It is likely that the behavior of aldehydes towards resorcin in the presence of a trace of chlorhydric acid may be used as a test for that class of substances. Whether other groups of substance show the reaction will be made the subject of an examination. Of interest also will be the examination of the behavior of aldehydes towards aromatic hydrocarbons, and phthalic anhydride toward phenols, in the presence of a small quantity of a mineral acid.

Summary.

I. Mixtures of aromatic aldehydes and phenols are converted by mere traces of acids, more or less rapidly, according to the acid used, into white resins.

II. The resorcin-benzaldehyde resin is converted by the further action of dilute acids into two crystalline compounds, one of which is isomeric with the resin when the latter is dried at 100°.

III. Fixed alkalies and potassium carbonate convert a mixture of resorcin and benzoic aldehyde into a resin.

IV. The properties of the crystalline compound $C_{26}H_{20}O_4$ resemble those of the so-called crystallisable resins. From its alkaline solution it is precipitated by acids in the form of a resin, which separates in form of the original crystals from the alcoholic solution.

V. The above results make it extremely probable that the formation of at least some of the resins in the vegetable world is due to aldehydes and phenols coming in contact with the contents of the cells, as both of these classes of compounds are undoubtedly among the products formed in plant-life.

TUFTS COLLEGE, MASS., *July* 3, 1883.

II.

BY A. MICHAEL AND A. M. COMEY.

The following experiments on the action of alkylaldehydes on phenols are considered as preliminary work of an investigation of the reaction in the manner stated in the preceding paper.

Action of Ethylaldehyde on Orcin and Resorcin.

A drop of chlorhydric acid added to a mixture of aldehyde and orcin causes no change in the cold; but when the solution is heated for a moment at 100°, a copious white precipitate is deposited. For the preparation of the substance, equal weights of aldehyde and orcin were dissolved in eight parts of absolute alcohol, and three drops concentrated chlorhydric acid added. The precipitate, formed on heating the solution for a minute at 100°, was filtered, washed out well with alcohol and then with water. For analysis it was dried at 100° in a current of CO_2.

0.190 gram of substance gave 0.5035 gram of CO_2 and 0.1240 gram of H_2O.

	Theory for $C_{18}H_{20}O_4$.	Found.
C	72.00	72.26
H	6.67	7.24

The substance has a slight yellowish color, and consists of small round plates. It is stable in the air at ordinary room-temperature; at 100° it rapidly takes a dark color. The usual organic solvents dissolve it neither in the cold nor in the heat. In alkalies it dissolves to form a solution that rapidly oxidises in the air. Although the formation of this substance may be represented by the general equation representing the action of aromatic aldehydes on phenols, its properties indicate that it has a more complicated constitution than the members of that class of substances:

$$2CH_3—CHO + 2C_6H_3(OH)_2CH_3 = C_{18}H_{20}O_4 + 2H_2O.$$

The action of ethylaldehyde on resorcin is similar to its action on orcin. A solution of equal parts of aldehyde and resorcin dissolved in three parts of alcohol, and several drops of chlorhydric acid, solidified on heating at 100° to a gelatinous mass. It was pressed out between bibulous paper, and then extracted with boiling alcohol. The substance is insoluble in the usual solvents. Heated to a high temperature it takes fire and burns like tinder. We were unable to obtain it in a state suitable for analysis, as it decomposed in a current of CO_2 at 100°.

Action of Chloralhydrate on Resorcin.

When an aqueous solution of chloralhydrate and resorcin is boiled in a flask connected with an inverted cooler, it gradually takes a darker color, and after some hours a crystalline precipitate begins to settle. We found that working according to the following directions gave the best yield: Five parts of the hydrate, ten parts of resorcin, and forty parts of water were heated for 12–24 hours in a flask connected with an inverted cooler. The light yellow crystalline product of the reaction separated in part from the boiling solution, and a further quantity on cooling; sometimes, however, not until the sides of the vessel were rubbed with a glass rod. A portion of the filtrate gave a copious precipitate of silver chloride on addition of silver nitrate, and the remainder yielded on continued boiling a second precipitate of the substance. From the amounts taken, about 2½ grams of the new substance were obtained. For analysis

it was recrystallised several times from dilute alcohol, and care was taken to avoid unnecessary heating in contact with the air. The substance does not contain chlorine. The analyses gave the following numbers:

I. 0.2418 gram of substance, dried *in vacuo*, gave 0.5632 gram of CO_2 and 0.0878 gram of H_2O.

II. 0.2632 gram of substance, dried *in vacuo*, gave 0.6170 gram of CO_2 and 0.1078 gram of H_2O.

III. 0.2393 gram of substance, dried *in vacuo*, gave 0.5600 gram of CO_2 and 0.0938 gram of H_2O.

	Theory for $C_8H_8O_3$.	Found. I.	II.	III.
C	64.00	63.53	63.93	63.82
H	4.00	4.03	4.54	4.35

The substance dried in a vacuum does not contain water of crystallisation; the air-dried compound did not lose in weight when heated in dry CO_2 at 100°. It separates from a solution in very dilute alcohol on cooling as fine, yellowish needles, which melt under decomposition at a high temperature. They are somewhat soluble in hot water, more easily in a boiling aqueous solution of resorcin, and are deposited on cooling as prismatic needles. In alcohol and acetic acid they are extremely soluble in the heat, moderately in the cold. The substance is very sensitive to the action of oxygen. It is, when pure, probably perfectly white; but exposure to the air for a few moments suffices to give it a yellowish tint. It dissolves in concentrated sulphuric acid, and the solution takes a beautiful blue color on exposure to the air. Alkalies dissolve it readily in the cold; the solution becomes brown almost immediately on exposure to the air, owing to the absorption of oxygen. After treatment of its alcoholic solution with nascent hydrogen the addition of water gave an almost white precipitate. This precipitate on drying, or when recrystallised, took a yellowish tint. A reduction had not taken place. This was proven by converting it into the acetyl derivative, and a comparison of its properties with those of the acetyl derivative of the original compound. These experiments make it probable that the product analysed was slightly oxidised. The substance is completely oxidised in the cold by potassium permanganate to carbon dioxide. An attempt was made, by adding a small quantity of permanganate at a time, to effect the isolation of intermediate products, but it was found that

part of the substance was completely oxidised while the rest remained unchanged.

To prepare the acetyl derivative 2 grams of the substance, 4 grams of acetic anhydride, and 1 gram of fused sodium acetate were heated for several hours at 100°. The solid substance dissolved on heating in the anhydride, and soon a separation of the new product began. The product of the reaction was extracted with water, and the residue crystallised several times from strong alcohol. On analysis the following numbers were obtained:

I. 0.2302 gram of substance, dried at 100°, gave 0.5210 gram of CO_2 and 0.0895 gram of H_2O.

II. 0.2350 gram of substance, dried at 100°, gave 0.5317 gram of CO_2 and 0.0988 gram of H_2O.

III. 0.2227 gram of substance, dried at 100°, gave 0.5065 gram of CO_2 and 0.0905 gram of H_2O.

	Theory for $C_6O_2H_4(OCCH_3)_2$.	Found.		
		I.	II.	III.
C	61.53	61.71	61.70	61.20
H	4.27	4.32	4.67	4.51

The compound separates from alcohol as white, prismatic crystals that melt at 159°. It is insoluble in hot water, moderately soluble in hot alcohol, but slightly in cold. In alkalies it is insoluble in the cold; when heated a gradual solution was effected. The substance is very stable towards oxygen, and may be heated in the air to 120° without undergoing any change. Its stability indicates that the instability of the mother-substance towards oxygen is due to oxidation beginning at its hydroxyl.

The chloral-resorcin compound can be heated with benzoylchloride to 100° without a reaction ensuing; at 120° an evolution of chlorhydric acid begins. A mixture of the substance and benzoylchloride, in proportion of one mol. to five, was heated at 120° until the disengagement of chlorhydric acid ceased. The product of the reaction was boiled out several times with water, and the insoluble residue crystallised four times from alcohol. An analysis gave the following numbers:

0.2158 gram of substance, dried at 100°, gave 0.5827 gram of CO_2 and .0868 gram of H_2O.

	Theory for $C_6O_2H_4(OCC_7H_5)_2$.	Found.
C	73.74	73.62
H	3.91	4.47

The substance separates from alcohol as small crystals, which have a slight pinkish tint. They melt at 165°. In boiling water they are insoluble, moderately soluble in hot alcohol, nearly insoluble in cold.

The formation of the compound $C_8O_3H_6$ from chloralhydrate and resorcin may be represented by the following equation:

$$C_6H_4(OH)_2 + 2CCl_3—CH(OH)_2 = C_8H_6O_3 + CCl_3COOH + 3HCl + H_2O$$

The examination of the substance is not sufficiently advanced to allow an insight into its constitution, more than as follows from the experiments on the action of acetic anhydride and benzoylchloride, that it contains two hydroxyl. We consider it useless, under these circumstances, to offer any suggestion regarding its constitution, but reserve the right to return to the subject later in the investigation. Chloralhydrate and orcin yield a similar compound, melting at 250°, whose acetyl derivative melts at 190°. This compound is more stable towards oxygen than the resorcin compound. It is probable that corresponding derivatives of other phenols can be obtained in a similar manner.

TUFTS COLLEGE, MASS., *July* 5, 1883.

LABORATORY NOTES.—III.[1]

BY ARTHUR MICHAEL.

X.—SOME CONVENIENT QUANTITATIVE LECTURE APPARATUS.

The need felt by teachers of chemistry not only to present to their hearers the principal facts of their science qualitatively, but also quantitatively, has been the cause of what may be called an evolution in lecture apparatus. This has culminated in instruments, notably by Bunsen and A. W. Hofmann, which are hardly open to improvement as far as simplicity combined with accuracy are concerned. Their deficiency is more in expensiveness, and, especially in regard to Hofmann's apparatus, fragility. In this note some quantitative lecture apparatus will be described, which were devised with the special view of combining sufficient accuracy with stability

[1] This Journal, **1**, 413; **5**, 192.

and cheapness. It is becoming more and more desirable that all students of chemistry should convince themselves of the truth of the most important reactions, and the composition of some of the principal inorganic compounds, from personal observation, and apparatus has become imperative which can be made by any one having a slight experience in glass-blowing. The aid that a knowledge of glass-blowing affords to a scientific chemist cannot be overestimated. The writer is convinced that a training in it should never be omitted from the course required of students making chemistry their profession.

The trough used is Liebig's well-known instrument slightly modified. Liebig's trough has notably two defects. The eudiometer after the explosion is apt to bump, which often causes an overflow of mercury, and even at times breaking the apparatus. This is remedied by placing a rubber plug on the bottom of the trough, and holding the eudiometer firmly down on it by means of a retort-clamp. A second defect is in the difficulty of emptying, or adjusting the height of the mercury, even when it does not contain a eudiometer. To obviate this inconvenience a tubulus is brought on the narrow part of the trough, an inch or two above the foot, and fitting into it a cork with a tube bent at right angles and ending in a piece of rubber tubing and spring-clamp[1] (Fig. 1). The cup of the trough should be three or four inches in diameter, while the narrow part need not be much wider than the largest eudiometer in use. These additions, as slight as they may seem, quite change the apparatus in respect to convenience and handiness.

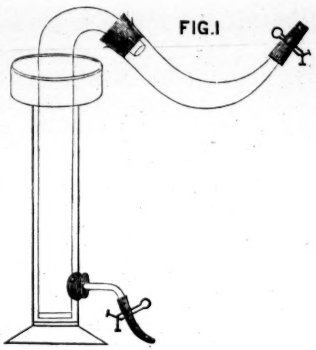


FIG. 1

The eudiometers should be several inches higher than the trough, and may be conveniently divided by calibration into twelve equal

[1] A hole drilled by means of a diamond and fitted with a cork and tube will answer the purpose. The described trough, as well as the other apparatus which will be mentioned, can be obtained of the Prang Educational Company, No. 7 Park Street, Boston, Mass.

divisions. In order to render the readings noticeable from a distance, rings of dark rubber are placed over each division. A rubber band, about one-half inch in width, brought over the open end of the eudiometer, will be found to render it less liable to breakage, and is also of use in indicating the proximity of the open end to the surface of the mercury. To obviate the necessity of lowering the eudiometer a number of times while introducing a given volume of gas, it has been found desirable that each instrument should have a second calibration, which is made by introducing successively a unit volume of air, when the eudiometer is held upright, with the upper end of the broad rubber band level with the mercury in the trough. The results are marked in half-lines across the instrument, with the number of unit volumes.

In the analysis of gases requiring an absorption of part of the products formed by the explosion a modified eudiometer is used, which obviates the introduction of liquid reagents. The instrument ends in a tube bent in the form of a half-circle, and connected by a rubber tube with a small bulb (Fig. 2). After the explosion, the communication between the eudiometer and the bulb containing the absorption-liquid is opened, and the eudiometer sunk to the bottom of the trough. Owing to the gases being under pressure, the absorption takes place quite rapidly, and is generally finished in one-half to three-quarters of an hour, when the spring-clamp is closed and a second reading taken. The instrument has the further advantage of permitting the examination of the absorption liquid.

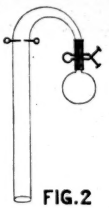


FIG. 2

Bunsen[1] has devised a very ingenious apparatus for the purpose of ascertaining the composition of certain oxides by measuring the volume of oxygen used in oxidising a known weight of the element. The following apparatus involves the principle of Bunsen's, but is much more compendious and needs less mercury, without a very great loss in the accuracy of the results. A tube about an inch longer than the trough is graduated, beginning an inch and a-half from the upper end, into about 160–180 parts of 1 cc. each. The upper end of the measuring tube is joined to a tube of about three-fourths of its diameter, and bent to form an angle of 45°. This tube is connected by a rubber cork with a curved tube of difficultly fusible

[1]See Heumann, Anleitung zum Experimentiren bei Vorlesungen über anorganische Chemie, 52.

combustion tubing, which is drawn out at the other end to a small tube, and closed by a piece of tubing and spring-clamp (Fig. 1).

In the analysis of sulphur and carbon dioxides, when the volume of the gas after the combustion remains unchanged, the apparatus is about half filled with oxygen. This is done by connecting the open end of the heating-tube with an oxygen generator, displacing the air, then the measuring-tube brought under mercury to 100 cc., the generator disconnected and the heating-tube closed. By heating the carbon or sulphur, which is previously placed in the heating-tube—the first, to prevent the tube from cracking on a piece of platinum foil, the latter on a chip of glass—a vivid combustion takes place, which can be seen from a distance. In the analyses of oxides, when the volume after combustion is less than the volume of oxygen taken, the measuring-tube is filled with oxygen to about 20 cc. from the open end, and a quantity of the element used which requires from 100 to 120 cc. of oxygen for its combustion. Before heating the substance, the measuring-tube is firmly placed on the rubber plug of the trough, which is then filled with mercury. The results obtained in the analyses of phosphorus pentoxide,[1] arsenic trioxide, magnesium oxide, &c., are sufficiently accurate to prove the constitution of these compounds beyond a doubt.

Bunsen's apparatus has hitherto only been used in ascertaining the volume of oxygen required for the combustion of certain elements. The above-described apparatus, or a slight modification of it, can be used for ascertaining the composition of a large number of important inorganic compounds, by measuring the volume of gas evolved in the decomposition of a known weight.

In studying quantitatively the decomposition of a substance, potassium chlorate for instance, by heat, a weight of it which will give off about 120 cc. of gas is placed on a small platinum boat and brought into the heating-tube. After the mercury is adjusted opposite the zero mark, the substance is heated by a Bunsen burner until the volume of gas in the measuring-tube remains constant, when, after cooling, a second reading will give the volume of gas evolved in the reaction.[2]

[1] Amorphous phosphorus must, of course, be used in this experiment. The commercial product leaves an ash, which is insoluble in water. It is therefore necessary to purify it, or determine the ash and make the required correction.

[2] It is well to add a trace of platinum black in the analysis of $KClO_3$. A much smaller heating tube closed at one end, and the bent open end fitted into the measuring tube, is advantageously used in such pyro-analyses. That the measuring tube and trough can be replaced by an apparatus constructed on the U tube principle is evident.

For the purpose of estimating the volume of a gas given off in a wet reaction, the heating-tube is replaced by a small flask of a capacity of 20–30 cc., and connected by a tube, attached to the neck and bent at right angles, to a drying tube. Through a rubber cork in the flask, a glass rod bearing a small perforated platinum basket and marked when the basket is in the upper part of the flask, is brought, and the rod greased that it may be freely moved in the cork. The drying tube is filled with calcium chloride, and connected by a rubber cork with the measuring-tube (Fig. 3). If the gas is soluble in the liquid used for decomposition, the flask is replaced by a small test-tube, on which a mark is brought showing that two or three cc. of the liquid are used, and a correction made for solubility. For analysis the flask is half-filled with the liquid, the glass rod pressed down until the mark is in contact with the upper end of the cork; and after the volume of air in the measuring-tube is read, the basket, containing a weighed quantity of the substance, is brought under the liquid. After the reaction is over the rod is brought back to the original position, and from a second reading the volume of gas evolved is ascertained.

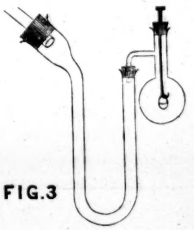


FIG. 3

I have not entered into the details of handling the apparatus, because they do not essentially differ from those necessary in using an ordinary eudiometer. Before each reading, the mercury in and outside the measuring-tube is brought to a level, and barometric and thermal observations are, of course, necessary. It is evident that three classes of reactions may be quantitatively examined by means of the apparatus. Firstly, those depending on a volume of oxygen absorbed;[1] secondly, those in which a gas is evolved at the temperature under a red heat; and, finally, those reactions in which a gas is evolved in the action of a liquid on a solid. The important reactions which can be examined in the apparatus are so numerous that its range is hardly exceeded by any other lecture apparatus. In most cases the complete analysis may be realised in a few moments by a volumetric analysis of the product

[1] No experiments have been made as yet on reduction of heavy metallic oxides in hydrogen, under similar conditions; but I do not doubt that sufficiently accurate results would be obtained.

remaining in the heating-tube or decomposition flask. Thus, in the analysis of potassium chlorate, the chloride remaining in the heating-tube can be washed into a beaker and a volumetric chlorine estimation made; or, in the investigation of the action of chlorhydric acid on metallic zinc or calcium carbonate, a known volume of standard acid taken and the undecomposed acid determined by titration.

It is often desirable to keep a small volume of a gas for subsequent investigation—a purpose for which the following simple gasometer has been found useful: Two small bottles, of about 50 cc. each, are fitted with double-bored rubber corks, and connected by a glass tube bent in the form of a syphon. The limb of the syphon, which is in the flask used as gasometer, is somewhat longer than the other limb. Through the second hole of that bottle a bent delivery tube, provided with a small glass stopcock, barely passes, and a small bent tube passes through the cork of the second bottle. For use, the gasometer and syphon are filled with mercury, and the end of the delivery tube then connected with the generating flask.[1] A small quantity of mercury is allowed to remain in the gasometer. The apparatus works, to a certain extent, automatically. On opening the stopcock of the charged gasometer, mercury will pass over until it is on a level in both bottles, and the remaining half can be expelled by applying pressure to the bent tube of the second bottle. A well-constructed apparatus will keep a gas for weeks without an appreciable change.

I wish finally to call attention to a slight modification of Hofmann's well-known V tube, which permits the collection of both the products of decomposition, and can, therefore, be used for quantitative analysis. On the upper side of the bend of the tube a glass tube is connected, which is an inch higher than the limbs of the V tube (Fig. 4). The limbs are graduated in five or six equal parts; those on the open limb beginning, not at the open end, but about one half an inch from it. For use, the apparatus is filled with liquid, and the cork, through which a glass

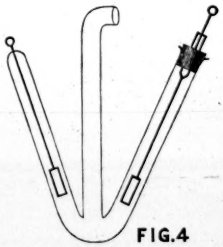


FIG. 4

[1] A more advantageous form is to have the delivery tube connected to the neck of the gasometer, directly under the rubber cork.

tube with platinum electrode passes, is pressed into the open limb until it reaches the first graduation. The displaced liquid flows out through the middle limb, which is conveniently connected with a rubber tube. Ungraduated Ure's eudiometers, provided with a short horizontal tube on the lower side of the bend, or on the upper side and bent downwards, make a cheap and efficient substitute for Hofmann's lecture-eudiometer, especially for students' use in the laboratory.

XI.—OBSERVATIONS ON THE ACTION OF ACETYLCHLORIDE AND ACETIC ANHYDRIDE ON CORN AND WHEAT STARCH.

The following preliminary experiments on the action of acetic anhydride and acetylchloride on corn and wheat starch were made with a view of ascertaining whether the typical physical differences of these varieties of starch are noticeable in their acetyl derivatives. According to Schützenberger,[1] starch heated with acetic anhydride at 140° yields an amorphous triacetyl derivative.

I. Two grams (1 mol.) of potato starch and 5 grams (4 mols.) of acetic anhydride were heated in a closed tube at 148–152° for two hours. The starch was converted into the acetyl derivative. It did not give a coloration with iodine solution; but after boiling with alkaline solutions it gave the blue starch test, showing that starch was regenerated. The granules, under the microscope, could not be distinguished from the original potato granule. The acetyl compound is insoluble in acetic acid, but on continued boiling a gradual solution is effected. The addition of water precipitates an amorphous white substance, which is soluble in hot alcohol and cold acetic acid.

A second tube prepared like the first with the difference that corn starch was used, was also heated for two hours at 148–152°. The properties of this acetyl derivative are like those of corresponding derivative of the potato granule, but it had the form of the corn granule. It is evident from these experiments that the characteristic forms of the potato and corn granules are not changed when these starch-varieties are acetylised.

II. Two tubes were prepared like the above, excepting that anhydride containing 10 per cent. of acetic acid was used, and heated at

[1] Ann Chim. Phys. [4], **21**, 235.

158–160°. The granules of acetyl corn starch appeared somewhat flattened and were not sharply defined. They still retained, however, the general appearance of the corn granule. The granules of acetyl potato starch retained their sharp contour; but were, perhaps, slightly enlarged. After heating with water they appeared flattened and lost their well-defined form.

III. Two grams of corn starch and five grams of acetylchloride were heated for fifteen hours at 55–58°. The tube on opening gave off a considerable quantity of chlorhydric acid. Continued heating did not cause a further formation of chlorhydric acid. The contents of the tube was extracted with chloroform, filtered from insoluble, undecomposed starch, and the chloroform of the filtrate driven off by heating on a water-bath. The residue was then dissolved in alcohol, treated with bone black, and gave on cooling a grayish white precipitate, which melted at 144°. Redissolved in warm, dilute alcohol, a white amorphous substance separated on cooling, which began to soften at 148°, and had the constant melting-point of 150–151°. The first alcoholic filtrate gave on concentration no further precipitate, but on addition of water a white amorphous substance separated, which on crystallisation from very dilute alcohol gave a substance sinking together at 126°, and melting at 128–129°. Acetylchloride has evidently quite a different action on starch than acetic anhydride. The substance melting at 150° is probably not an acetyl derivative of starch, but of one of the dextrine modifications. The substance melting at 129° is very likely formed secondarily by the action of hot alcohol on the first product. A second tube prepared as the above, but on the treatment of its contents, unnecessary heating with alcohol and bone-black avoided, gave only a trace of the product melting at 129°.

A tube containing potato instead of corn starch, and subjected to the same conditions, gave similar results. A slight difference in the properties of the acetylised compound is noticeable, but I do not think that they warrant a conclusion as to chemical differences in the properties of the two products. The substance had a slight brown color, and, sinking together at 145°, melted at 146–148°.

TUFTS COLLEGE, MASS., *July 16th*, 1883.

RESEARCHES ON THE COMPLEX INORGANIC ACIDS.[1]

By Wolcott Gibbs, M. D.

Rumford Professor in Harvard University.

[Continued from Vol. 3, p. 416.]

The compounds which I have hitherto described may be embraced under the general formula—

$$m\mathrm{RO_3}.2\mathrm{R'_2O_5}.p\mathrm{R''_2O},$$

in which m may represent any even number from 10 to 48 inclusive, p the number of molecules of base (old style), R an atom of tungsten or molybdenum, and R′ one of phosphorus or arsenic. I shall now proceed to show that these results may be generalised in a variety of different ways, and, further, that there are other typical formulas, perhaps less general than that above given, but still embracing many interesting and instructive special cases.

HYPOPHOSPHO-MOLYBDATES.

Hypophospho-molybdate of Ammonium.—When solutions of 14:6 acid ammonic molybdate and sodic hypophosphite are mixed, no precipitate is formed, but the liquid takes a fine blue color from the partial reduction of molybdic teroxide to $\mathrm{Mo_2O_5}$. On addition of chlorhydric acid and stirring for a short time, a large quantity of a crystalline salt separates. This is to be filtered off, well drained by the filter-pump, and washed with cold water, in which it is not very soluble. When perfectly pure and free from $\mathrm{Mo_4O_5}$ the salt presents colorless prismatic crystals, which are readily soluble in hot water. The solution, at first pale blue, speedily assumes a deeper tint; with cold water a colorless strongly acid solution may be obtained, and with such the reactions here given were obtained. Baric chloride gives no precipitate alone, but after adding ammonia a colorless salt is thrown down, which is at first flocky, but which soon becomes fine-grained granular-crystalline. Strontic and calcic chlorides behave in a similar manner, but the calcic precipitate does not form so rapidly. Manganous sulphate gives no precipitate alone, but after adding

[1] Communicated by the Author, from the Proceedings of the American Academy of Arts and Sciences.

ammonia a white flocky salt is formed, which becomes yellowish on standing. Cupric sulphate behaves in the same manner; the precipitate after the addition of ammonia is green and flocky. The mixture with solution of copper is not reduced on boiling, either alone or after addition of chlorhydric acid. The solution of the hypophospho-molybdate gives a canary-yellow precipitate with mercurous nitrate, and a nearly white precipitate with argentic nitrate, which soon becomes gray and finally black. Thallous nitrate gives a white flocky precipitate. When the dry salt is heated, it becomes at first black and fumes slightly, but on further heating it melts to a dark blue mass which gives off a little molybdic teroxide on heating to redness. The fused mass dissolves readily in hot water, forming a deep blue solution which has an acid reaction, and gives with magnesia-mixture the characteristic ammonio-magnesic phosphate. The effect of heat is represented by the equation

$$8MoO_3.2[H_2.PO.OH].2(NH_4)_2O + 2H_2O = 8MoO_3 + P_2O_5 + 3H_2 + 2(NH_4)_2O + H_2O.$$

In the analyses the loss by ignition corresponds to $2(NH_4)_2O + H_2O + 3H_2$, and the residual mass to $8MoO_3 + P_2O_5$, when the ignition is made with sodic tungstate. In this salt—

1.3172 gram lost on ignition with WO_4Na_2 0.1329 gram = 10.09 per cent. H_2O, $(NH_3)_2O$, and H.

1.0764 gram lost on ignition with WO_4Na_2 0.1086 gram = 10.09 per cent. H_2O, NH_3, and H.

1.2369 gram gave 0.1836 gram NH_4Cl = 7.21 per cent. $(NH_4)_2O$.

1.2850 gram gave 0.0918 gram $(NH_4)_2O$ by titration = 7.15 per cent. $(NH_4)_2O$.

2.4322 grams gave 0.3860 gram $P_2O_7Mg_2$ = 9.42 per cent. PO_2H_3.

1.6217 gram gave 0.2578 gram $P_2O_7Mg_2$ = 9.30 per cent. PO_2H_3.

The analyses lead to the formula

$$8MoO_3.2[H_2.PO.OH]2(NH_4)_2O + 2Aq,$$

which requires:

		Calc'd.	Mean.	Found.	
$8MoO_3$	1152	80.89	80.97	...	...
$2PO_2H_3$	132	9.27	9.36	9.42	9.30
$2(NH_4)_2O$	104	7.31	7.18	7.21	7.15
$2H_2O$	36	2.53	2.49	2.47	2.52
	1424	100.00	100.00		

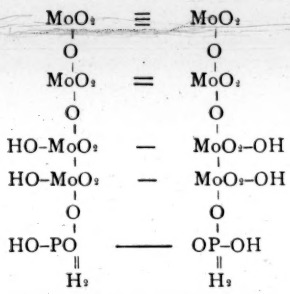
In computing the results of the analyses the loss of weight by ignition, 10.09 per cent., is of course taken to represent $2(NH_4)_2O + H_2O + 3H_2$, in accordance with the equation given above. In the analyses the quantity of hypophosphorous acid was determined by dissolving the salt in a solution of sodic carbonate, and then adding bromine, which with the aid of heat readily converts the hypophosphorous into phosphoric acid. The quantity of the former could not be determined by means of potassic hypermanganate in an acid solution. Bromine does not act sensibly upon acid solutions, and even an excess of nitric acid effects an imperfect oxidation. These facts, taken in connection with the relations of the salt to solutions of copper and silver, seem to show that the stability of hypophosphorous acid is increased by its combination with molybdic teroxide. The salt has, as stated, a strong acid reaction, and the limit of the basicity of this class of compounds still remains to be determined. The formula may also be written:

$$8MoO_3.2[H_2.PO.(NH_4O)_2]2H_2O + 2Aq.$$

The constitution of hypophosphorous acid was first established by Würtz. More recent investigations in organic chemistry have shown that it is to be regarded as dihydryl-phosphinic acid, and that it forms the initial term and type of an extensive series of organic acids, in which the two atoms of hydrogen attached to the phosphorus are replaced by methyl, phenyl, &c., and in which also arsenic may replace phosphorus. I do not propose at present to proceed further in this particular line of research, but will content myself with the statement that a solution of dimethyl-arsinic (cacodylic) acid gives immediately in one of 14:6 acid ammonic molybdate a beautiful colorless crystalline precipitate. It can hardly be doubted that this is a dimethyl-arsino-molybdate belonging to the general type represented by the formula

$$mMoO_3.2[(CH_3)_2.AsO.(OH)]n(NH_4)_2O.$$

The structural formula of the hypophospho-molybdate above described, or rather of the corresponding acid, may be written, in accordance with the general principles already assumed, as follows:



In this formula the acid is supposed to correspond to the ammonium salt described.

HYPOPHOSPHO-TUNGSTATES.

The salts of this series are not very well defined as regards their physical properties, and it is difficult to obtain any single one in a state of perfect purity. They are most readily prepared by boiling acid tungstates with a solution of hypophosphorous acid, and appear to be in general very soluble in water, yielding sometimes thick syrupy liquids, and sometimes gelatinous masses more or less colored by the partial reduction of tungstic teroxide.

Potassic Salt.—When a strong solution of hypophosphorous acid is mixed with one of 12:5 acid sodic tungstate, the liquid becomes turbid and yellowish, and after a short time gelatinises to a pale yellow mass. This is to be dissolved in boiling water, and a solution of potassic bromide added, which after a short time gives a white crystalline precipitate, to be drained upon the filter-pump, redissolved in hot water, again crystallised, drained, washed with cold water, and dried on woollen paper. As thus prepared, the salt presented small colorless granular crystals, soluble in hot water to a somewhat turbid strongly acid liquid, which effervesced with alkaline carbonates. The solution gave no precipitate with cupric sulphate, and no copper was reduced on boiling either with or without chlorhydric acid. Argentic nitrate gave a turbid white solution; on boiling, silver was reduced. Mercurous nitrate gave a white flocky precipitate, which on boiling became yellow, and finally dirty greenish yellow, without reduction of mercury. Baric

chloride gave a white precipitate of indistinct feathery crystals. When heated in a porcelain crucible the salt became blue, and finally white, giving off a sharp acid smell. The residue dissolved in water, in part at least, forming a strongly acid solution. Of this salt—

1.2295 gram lost on ignition 0.0340 gram = 2.76 per cent. water and hydrogen.

1.2295 gram gave 1.1172 gram $WO_3 + P_2O_5$ = 90.84 per cent.

0.7272 gram lost on ignition with WO_4Na_2 0.0203 gram = 2.79 per cent.

1.5110 gram gave 0.1921 gram $P_2O_7Mg_2$ = 7.57 per cent. PO_2H_3.

The analyses lead to the formula

$$18WO_3.6[H_2.PO.OH]4K_2O + 7Aq,$$

which requires:

		Calculated.		Found.	
$18WO_3$	4176	82.31	90.11	82.71	90.28
$6PO_2H_3$	396	7.80		7.57	
$4K_2O$	376	7.41		7.42	
$7H_2O$	126	2.48		2.45	
	5074	100.00		100.15	

In the analysis the hypophosphorous acid was determined by oxidation with bromine in an alkaline solution and precipitation with magnesia-mixture. The formula given may be written, with equal probability,

$$18WO_3.6[H_2.PO.OK]K_2O.3H_2O + 7Aq,$$

since the assignment of the fixed base is purely arbitrary; other arrangements are also possible. I am disposed to regard the salt as acid, with the formula

$$2(6WO_3.2[H_2.PO.OH]_2K_2O) + 6WO_3.2[H_2.PO.OH]_2H_2O + 5Aq,$$

so that the type of the corresponding acid, setting aside the question of basicity, will be

$$6WO_3.2[H_2.PO.OH]_2H_2O.$$

The structural formula of such an acid will be similar to that already given in the case of the hypophospho-molybdate described. Further investigation may, however, show that the more complex

formula must be admitted. I content myself with proving that there is at least one class of hypophospho-tungstates. In computing the direct results of the analyses I have assumed that, as in the case of the corresponding molybdenum compounds, the complex $2[H_3.PO.OH]$ is oxidised to P_2O_5 wholly at the expense of two molecules of WO_3 reduced to W_2O_5, which last is then again oxidised to $2WO_3$ by heating in air. This assumption appears to be justified by the changes of color observed on heating the salt. The actual loss of weight observed then corresponds to water and hydrogen only, the percentage of hydrogen being calculated from that of $P_2O_4H_6$.

When tungstic hydrate in excess is boiled with a solution of sodic hypophosphite, it dissolves very readily, giving a pale blue solution which yields on evaporation a thick syrupy liquid. This solution gives precipitates with $BaCl_2$, NH_4Cl, and KBr, and will furnish a convenient starting-point for further investigation. It does not oxidise readily in the air, even after long standing. A solution of dimethyl-arsinic acid gives with one of 12 : 5 acid sodic tungstate a beautiful colorless crystalline precipitate. I have not studied this compound, from want of proper facilities for work of the kind. It will, I think, prove to be a dimethyl-arsino-tungstate, coming under the general formula

$$m WO_3.2[(CH_3)_2.AsO.OH]nNa_2O,$$

and we may reasonably expect an extensive series of analogous compounds, in which other radicals take the place of methyl.

PHOSPHOROSO-MOLYBDATES.

Since phosphorous acid is now to be regarded as hydryl-phosphinic acid with the formula

$$[H.PO.(OH)_2],$$

the existence of a class of phosphoroso-molybdates and of phosphoroso-tungstates appeared, to say the least, a probable inference from that of the hypophospho-compounds already described.

Phosphoroso-molybdate of Ammonium.—When a solution of phosphorous acid—as prepared by the reaction of phosphorous chloride with water—is added to one of 14 : 6 acid ammonic molybdate, a very pale yellow indistinctly crystalline precipitate is formed, which is insoluble in cold water. Hot water dissolves it

only in a small proportion, but gives a milky emulsion, which settles very slowly. For analysis the salt was drained on a filter-pump, well washed with cold water, and finally dried on woollen paper. Of this salt—

1.9695 gram gave 0.0980 gram $(NH_4)_2O$ = 4.97 per cent. by titration.

1.1425 gram gave 0.0559 gram $(NH_4)_2O$ = 4.89 per cent. by titration.

0.9301 gram lost on ignition with WO_4Na_2 0.1225 gram = 13.17 per cent.

1.2722 gram gave 0.1374 gram $P_2O_7Mg_2$ = 7.97 per cent. PO_3H_3.

The analyses correspond fairly well with the formula

$$24MoO_3.4[H.PO.(OH)_2]4(NH_4)_2O + 17Aq,$$

which requires:

	Calculated.		Found.	
$24MoO_3$	80.41	88.04	79.88	87.85
$4PO_3H_3$	7.63		7.97	
$4(MH_4)_2O$	4.84		4.89	4.97
$17H_2O$	7.12		7.22	
	100.00			

The salt certainly contained a little phospho-molybdate, to which the faint yellow tint was probably due. It is very difficult to obtain a solution of phosphorous which is absolutely free from phosphoric acid. With respect to the formula I remark that the number of molecules of water may be purely accidental, and that there is at present no sufficient reason for rejecting the simpler expression—

$$12MoO_3.2[H.PO.(OH)_2]2(NH_4)_2O + xAq.$$

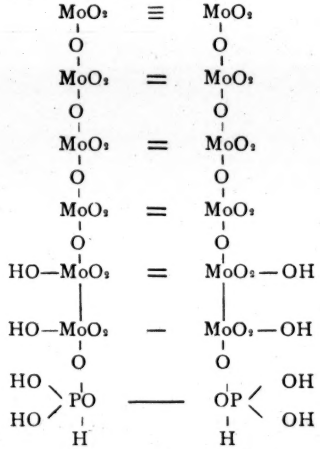
The type of the acid is then

$$12MoO_3.2[H.PO.(OH)_2]2H_2O.$$

A solution of baric chloride boiled with the phosphoroso-molybdate decomposes it more or less completely, giving a white very fine-grained crystalline salt. Under the same circumstances argentic nitrate gives a nearly colorless flocky substance, which quickly becomes darker, and finally assumes a dull violet color. Mercurous nitrate yields a clear pale yellow flocky salt; the phosphoroso-molybdate does not reduce a solution of mercuric chloride

even on boiling. Cupric sulphate dissolves the salt to a clear blue liquid. Manganous sulphate also dissolves it, forming a colorless solution. Alkaline hydrates dissolve it very readily to colorless liquids. The salt is readily decomposed by heating in a porcelain crucible, and fuses at a low red heat, giving off vapors of molybdic teroxide. The fused mass on cooling is bluish gray. It dissolves readily in water to a deep blue liquid, which has a strongly acid reaction, and gives with magnesia mixture the reaction for phosphoric acid.

The structural formula of the acid corresponding to the ammonium salt may be written provisionally:



If we accept the views now generally received as to the constitution of hypophosphorous and phosphorous acids, the hypophosphomolybdates, hypophospho-tungstates, and phosphoroso-molybdates furnish a much needed demonstration of the fact, that in this whole class of compounds part at least of the hydroxyl is united to phosphorus directly, and a part only to tungsten or molybdenum. This will appear at once from the formulas for the two acids, since these cannot be broken up into simpler expressions,

$[H_3.PO.OH]$, and $[H.PO.(OH)_2]$,

or from the structural formulas which I have given. I shall return to this point hereafter, and give additional proofs of the twofold mode of combination of hydroxyl.

Further investigation will almost certainly show that the homologues of hydryl-phosphinic or phosphorous acid will also form complex acids with tungstic and molybdic teroxides. Thus methyl-phosphinic acid [$CH_3.PO.(OH)_2$] should form at least one series of each of the general types:

$$m MoO_3.[CH_3.PO.(OH)_2]nH_2O.$$
$$n WO_3.[CH_3.PO.(OH)_2]pH_2O.$$

In these cases arsenic, and perhaps antimony, may replace phosphorus. Phosphoroso-tungstates may be formed by the action of phosphorous acid upon acid tungstates. The only salt obtained at present appears to have the formula

$$12WO_3.2[H.PO.(OH)_2]2K_2O + 12Aq.$$

I propose to return to this special point when describing the related groups of arsenoso-tungstates and antimonoso-tungstates and the corresponding molybdates. In the analysis of the phosphoroso-molybdate of ammonium the phosphorous acid was determined by dissolving the salt in an excess of a solution of sodic carbonate, oxidising with bromine, and precipitating with magnesia mixture.

VANADIO-MOLYBDATES.

The general analogy between vanadic, arsenic, and phosphoric pentoxides suggested to me the possibility of forming series of vanadio-molybdates and vanadio-tungstates, belonging to types of a character similar to those of the phospho-molybdates and phospho tungstates already described. I shall now show that such compounds may readily be formed by processes identical in principle with those which yield compounds of phosphoric and arsenic oxides with molybdic teroxide.

Vanadio-molybdates are formed when vanadic pentoxide V_2O_5 is digested with solutions of alkaline molybdates, more especially with the acid salts of potassium, sodium, or ammonium. The solution quickly becomes yellow, then, on heating, orange, and finally passes in many cases to deep orange-red. The vanadic oxide or acid employed must be perfectly free from vanadic dioxide, as this is also readily dissolved. The resulting compound then

belongs to the class of triple complex acids, and contains both oxides of vanadium united to molybdic oxide. I shall return to these compounds in due time, and meanwhile shall refer to them under the name of vanadico-vanadio-molybdates. The presence even of a small quantity of vanadic dioxide may usually be detected by a peculiar greenish shade of color, easily recognised when once seen. This tint disappears when the solution is heated for a short time with bromine water or nitric acid, which readily oxidise the lower oxides of vanadium.

Vanadio-molybdates are also formed when solutions of alkaline vanadates and molybdates are heated together, and more readily when an excess of acid is present. The mixed solution then assumes at once a deep orange-red color.

The same salts are also formed when molybdic oxide, MoO_3, is boiled with a solution of an alkaline vanadate or meta-vanadate. Ammonic meta-vanadate, VO_3NH_4, may now be had in commerce in a state of very considerable purity, and has served as the starting point for much of my work. A solution of this salt readily dissolves molybdic oxide, forming one or more vanadio-molybdates, only in this case there is a tendency to a kind of supersaturation, a large excess of molybdic oxide being dissolved and separating from the liquid on cooling.

Finally, vanadio-molybdates may be formed by the decomposition of phospho-vanadio-molybdates, a class of triple compounds also to be described.

The vanadio-molybdates of the alkaline metals are in general readily soluble in water. They are highly crystalline, have a yellow or greenish-yellow, sometimes orange-yellow or orange-red color, and give in many cases crystalline precipitates with salts of the alkaline earths, of silver, and of thallium. They are not decomposed by boiling with excess of acid, and are usually very stable, except in the presence of reducing agents.

Analytical Methods.—The quantitative separation of molybdenum from vanadium presented a new problem in analytical chemistry, the solution of which cost much time and labor. It may be effected in two different ways. When the vanadium is wholly or partially in the form of vanadic dioxide, VO_2, it is to be oxidised by heating the concentrated solution with nitric acid. An alkaline carbonate is then to be added until the solution is nearly neutral, when the vanadic and molybdic oxides may be precipitated together

by means of mercurous nitrate and mercuric oxide, precisely as in the estimation of tungstic oxide already described. The precipitate of mercurous vanadate and molybdate and mercuric oxide is to be filtered upon a paper filter. After drying, the filter and contents may be heated together in a platinum crucible, with free access of air. When the process is carefully conducted, the filter may be completely incinerated with great ease, and without loss of molybdic oxide from volatilisation. A weighed quantity of fused and pulverised neutral sodic tungstate is then to be added, when the crucible may be heated to redness, and the mercurous and mercuric oxides completely expelled. A second heating and weighing are always advisable. In this manner the sum of the weights of molybdic and vanadic oxides is obtained. To determine the quantity of vanadic oxide alone, the same process is to be repeated; only after burning off the filter the mass is to be carefully heated with a free supply of air to act mechanically until the whole of the molybdic oxide is volatilised and vanadic oxide remains as an orange-brown liquid, and, after cooling, as a crystalline mass. The complete expulsion of the molybdic oxide requires long heating, at a full red heat. The vanadic oxide is not volatile, but it has the inconvenient habit of creeping up the sides and over the edge of the crucible—a habit for which there appears to be no remedy. The weight of the molybdic oxide may then be determined by difference. This method gives good results, and in some cases may be used with advantage.

Another method is the following, which applies directly to the vanadio-molybdates of the alkaline metals, and to those of the alkaline earths, after the separation of the base. Ammonia is to be added in excess to the solution, which is then to be boiled for a few minutes, so as to convert the salt into a mixture of an alkaline vanadate and molybdate. A saturated solution of ammonic chloride is then added in very large excess, after which the liquid must be concentrated by continued boiling until reduced to a relatively small volume. The solution must then be allowed to stand for twenty-four hours, when a greater or less deposit of ammonic metavanadate will have formed in colorless crystals.[1] These crystals are to be brought upon an asbestos filter, and washed with a cold

[1] The best commercial chloride of ammonium always contains iron not precipitable by ammonia. If bromine water be added first to the boiling solution, ammonia in small quantity separates the iron completely.

saturated and pure solution of ammonic chloride. The vanadic pentoxide may then be found by carefully igniting the salt with free access of air. It is, however, better to dissolve the salt upon the filter with boiling water, reduce the solution by means of a current of sulphydric acid gas after adding a little sulphuric acid, filter, and titrate with potassic hypermanganate. The clear blue solution contains vanadic dioxide only. The end reaction is tolerably sharp in dilute solutions—say 0.25 gram—of VO_2 in 250 cc. of water. The reason for adopting the method of titration is, that the ignition of ammonic meta-vanadate, even when conducted with great care, usually yields a mixture of vanadic pentoxide and dioxide, which it is difficult to oxidise completely. The precipitation of ammonic meta-vanadate by ammonic chloride is, as is well known, not absolutely complete, but the results of the analyses are on the whole fairly good.

It is sometimes more advisable to employ a combination of the two methods described. After precipitating the two oxides by means of mercurous nitrate and mercuric oxide, the greater part of the molybdic oxide may be expelled by heat, after which the mixture of oxides, which now consists chiefly of vanadic pentoxide, may be dissolved in ammonia and treated with ammonic chloride in the manner above described. The quantity of molybdic oxide is most easily estimated by difference, the sum of the weights of the two oxides being determined by the method given above. It is not possible to reduce the vanadic pentoxide in the vanadio-molybdates to vanadic dioxide by means of sulphydric acid gas, by sulphurous oxide, or by any other reagent which I have tried, without at the same time reducing a portion of the molybdic teroxide to the blue oxide Mo_3O_8. This difficulty may, however, be overcome by first adding phosphoric acid to the solution in quantity about equal to the weight of the salt analysed. After the addition of a little sulphuric acid the reduction of the vanadic pentoxide may be effected either by boiling with a solution of sulphurous oxide, or by passing sulphydric acid gas for some time through the hot solution of the salt.

In separating vanadic from molybdic oxide by means of ammonic chloride it is necessary to keep the solution always slightly alkaline by the occasional addition of a little ammonia, since, as soon as the liquid becomes acid by the dissociation of the ammonium salts present, a vanadio-molybdate is again formed in greater

or less quantity. To resolve a vanadio-molybdate into a mixture of vanadate and molybdate, it is necessary to employ an excess of free ammonia, and also to heat the solution. Actual boiling is most advantageous.

Another method of estimating vanadic oxide in the presence of molybdic teroxide consists in boiling the compound with strong chlorhydric acid, passing the chlorine set free into a solution of potassic iodide, and then determining the free iodine volumetrically by sodic hyposulphite and starch. I have not actually employed this method, however, though it gives excellent results in the analysis of the vanadio-tungstates.

It will be convenient to speak in this place of the best method of determining vanadium in alkaline vanadates without special reference to its separation from other elements. I find that this estimation may be effected with great accuracy by first oxidising any lower oxide which may be present by means of nitric acid to vanadic pentoxide, and then precipitating the faintly acid solution by mercurous nitrate and an excess of mercuric oxide at a boiling heat. Precipitation by mercurous nitrate alone was long since suggested by Berzelius, but the addition of mercuric oxide to render and to keep the solution neutral makes precisely the difference between a very accurate and an only tolerably good result. The precipitate may be collected upon a paper filter, and after washing with hot water ignited with free access of air. On cooling, a fine orange-brown crystalline mass of vanadic pentoxide remains. The filtrate from the precipitated oxides contains no appreciable trace of vanadium. The great facility with which a solution of vanadic pentoxide containing free chlorhydric acid is reduced by ferrous salts, suggested the possibility of determining vanadium by titration with ferrous sulphate, a solution of potassic ferricyanide being employed to determine the point of complete reduction.

A special study of this process was made in my laboratory by my assistant, Mr. Charles A. French, to whom the following details are exclusively due. The solution containing vanadic pentoxide is to be concentrated, and chlorhydric acid solution containing about one-tenth of its weight of pure acid added in large excess. After nearly saturating with a solution of ferrous or ammonio-ferrous sulphate of known titre, the solution is to be heated nearly to boiling, and the titration then completed with the ferrous salt, the end reaction being determined by trial drops upon a porcelain plate with a

very dilute solution of potassic ferricyanide. Of this solution two drops of the ordinary laboratory reagent in a test-tube full of water give an appropriate strength. The process may be varied by adding the ferrous solution in excess, then titrating back by means of potassic dichromate of known titre, and finally adding the ferrous salt until the end reaction with ferricyanide is obtained. The ferrous solution may contain with advantage 0.005 gram of iron in one cubic centimeter. A sample of potassic divanadate containing no other impurity than a little potassic nitrate gave, by the gravimetric process above described, 65.12 per cent. V_2O_5. In three successive titrations with ammonio-ferrous sulphate Mr. French found 65.16, 65.27, and 64.95 per cent.

As ammonic meta-vanadate is now largely used in the manufacture of aniline black, and has become an article of commerce, the method of titration described above may perhaps find useful application in technical laboratories, as the end reaction in titrating with hypermanganate is not very sharp. I have in my work employed it in several cases as a check upon other methods.

In the analyses of vanadio-molybdates it is best to determine the alkalies by difference, as in the cases of the phospho-molybdates and phospho-tungstates. As in these cases also ammonia and water are best determined together by ignition with a weighed portion of neutral sodic tungstate, WO_4Na_2, a method suggested by Dr. F. A. Gooch for the whole class of phospho-tungstates and phospho-molybdates of ammonium; only in the case of the vanadio-molybdates and other salts containing both molybdenum and vanadium, it is necessary to be especially careful in igniting with the tungstate, because molybdic teroxide is sometimes given off before the complete fusion of the tungstate with the salt.

6 : 1 *Series.*—A solution of ammonic meta-vanadate, VO_3NH_4, readily dissolves molybdic teroxide on boiling, forming a deep orange-yellow solution. The liquid on standing deposits a very beautiful lemon-yellow salt, in sharp octahedral crystals, which are soluble in a rather large excess of cold water without sensible decomposition. The solution, on spontaneous evaporation, yields the salt without change. Of this salt—

1.1349 gram lost on ignition with WO_4Na_2 0.1806 gram = 15.91 per cent.

1.3220 gram lost on ignition with WO_4Na_2 0.2128 gram = 16.09 per cent.

1.5022 gram lost on ignition with WO_4Na_2 0.2412 gram = 16.05 per cent.

1.2477 gram gave 0.2201 gram NH_4Cl = 8.57 per cent. $(NH_4)_2O$.

1.3822 gram gave 0.2439 gram NH_4Cl = 8.57 per cent. $(NH_4)_2O$.

1.2847 gram gave 0.1893 gram V_2O_5 by $KMnO_4$ = 14.73 per cent.

The analyses lead to the formula

$$6MoO_3.V_2O_5.2(NH_4)_2O + 5Aq,$$

which requires:

		Calc'd.	Found.		
$6MoO_3$	864	69.62			
V_2O_5	183	14.74	14.73		
$2(NH_4)_2O$	104	8.39	8.57	8.57	
$5H_2O$	90	7.25	7.34	7.52	7.48
	1241	100.00			

The reactions of a solution of this salt in cold water are as follows: No precipitate with salts of copper, zinc, manganese, and cadmium. Argentic nitrate gives a flocky yellow precipitate, with a tinge of buff. Mercurous nitrate gives a bright yellow precipitate. Thallous nitrate gives a very pale yellow flocky precipitate, which does not become crystalline on standing. Baric chloride gives no precipitate at first, but after a short time very beautiful sharp octahedral crystals; after longer standing, small pale yellow very distinct prismatic crystals also appear in the solution. Strontic chloride gives, after some days, very well defined pale yellow prismatic crystals. The solution of the vanadiomolybdate gives a rather dull yellow flocky precipitate with hydrochloride of brucin, and a bright yellow one with hydrochloride of strychnin. No precipitate is formed at first with potassic bromide, but after some days beautiful very well-defined granular crystals are deposited in quantity.

The solution of the salt has a strongly acid reaction. The mercurous salt is decomposed by dilute chlorhydric acid, with formation of mercurous chloride and a yellow acid solution, doubtless of the acid of this series. The acid was decomposed by spontaneous evaporation, and did not yield crystals.

It appears unnecessary to give a structural formula for the salt described, since we may regard V_2O_5 as simply replacing P_2O_5,

and with the same function as this last, so that the structural formulas already given for the phosphotungstates will apply to the present case also.

Eight Atom Series.—When acid ammonic molybdate is dissolved, and vanadic pentoxide is added in small quantities at a time, the boiling solution quickly becomes yellow, and then orange. If the vanadic oxide is not perfectly free from dioxide, VO_2, a little bromine water should be employed to complete the oxidation. If a solution of baric chloride be mixed with the rather dilute and warm solution, no precipitate is formed at first, but after a few seconds an abundance of beautiful yellow well-defined crystals appears. These crystals are very sharp octahedra, and strongly resemble those of one of the ammonium salts of the six-molecule series. After a time granular yellow crystals make their appearance also in large quantity. The habitus of these crystals is so different from that of the first named that the two can readily be separated when mixed. A very approximate separation can also be effected by pouring off the liquid the moment that the granular crystals begin to appear. The yellow octahedral crystals are soluble in hot water, containing a little chlorhydric acid, and may be recrystallised. When heated, the salt swells up very much, and turns black, looking like coke. Of this salt—

1.0070 gram lost on ignition with WO_4Na_2 0.1310 gram = 13.00 per cent.

0.9716 gram lost on ignition with WO_4Na_2 0.1280 gram = 13.17 per cent.

1.2449 gram lost on ignition with WO_4Na_2 0.1637 gram = 13.16 per cent.

0.9682 gram gave 0.6534 gram $MoO_3 + V_2O_5$ = 67.48 per cent.

1.0162 gram gave 0.3029 gram SO_4Ba = 19.56 per cent.

1.0343 gram gave 0.3072 gram SO_4Ba = 19.50 per cent.

1.0190 gram gave 0.3023 gram SO_4Ba = 19.48 per cent.

1.0937 gram gave 0.0998 gram V_2O_5 = 9.12 per cent.

1.4395 gram gave 0.1356 gram V_2O_5 = 9.37 per cent.

These analyses lead to the formula

$$16MoO_3.2V_2O_5.5BaO + 29Aq,$$

or,

$$8MoO_3.V_2O_5.3BaO + 8MoO_3.V_2O_5.2BaO.H_2O + 28Aq,$$

which requires:

		Calculated.		Found.	
$16MoO_3$	2304	58.25		58.34	
$2V_2O_5$	364	9.21		9.12	9.37
$5BaO$	765	19.35	19.48		19.56
$29H_2O$	522	13.19	12.96	13.00	13.16
	3955	100.00			

The salt is therefore to be regarded as the acid salt of the eight-atom series, and belongs to a type of which several examples have been given among the phospho-tungstates and phospho-molybdates. It may also be considered as an acid sixteen-atom salt, upon the view which I have suggested in another place as at least possibly correct. The 16 : 2 barium salt is also formed when baric chloride is added to a solution of the 6 : 1 vanadio-molybdate of ammonium already described. The last-named salt is therefore formed when vanadic pentoxide is dissolved in acid ammonic molybdate, as well as when molybdic oxide is dissolved in ammonic meta-vanadate. In the double decomposition with baric chloride at least three molecules of the 6 : 1 ammonium salt must take part. The barium salt is nearly insoluble in cold water, but is soluble in much hot water, with partial decomposition and deposition of baric molybdate. The solution in cold water reddens litmus strongly; it gives with argentic nitrate a pale, and with mercurous nitrate a bright yellow flocky precipitate.

The first determination of vanadic pentoxide in this salt was made by heat alone, the mixture of molybdic and vanadic oxides being ignited until a constant weight was obtained. In the second analysis the determination was made by titration with ferrous sulphate after adding chlorhydric acid to the solution.

Eighteen Atom Series.—A boiling solution of ammonic meta-vanadate readily dissolves molybdic teroxide, MoO_3, forming a deep yellow or orange yellow solution. When the oxide is added as long as it is readily dissolved, an olive-green liquid is obtained, from which after twenty-four hours hard tabular crystals of a pale greenish color are deposited. These crystals are decomposed by boiling water, beautiful yellow needles very slightly soluble in water being formed, together with a greenish yellow solution which soon becomes turbid. The salt could not be purified by recrystallisation, and was therefore washed with a little cold water and dried on woollen paper. Of this salt—

0.8067 gram ignited with WO_4Na_2 lost 0.1586 gram = 19.66 per cent.

0.8538 gram gave 0.2140 gram NH_4Cl = 12.18 per cent. $(NH_4)_2O$.

1.0243 gram gave 0.2526 gram NH_4Cl = 11.99 per cent. $(NH_4)_2O$.

0.7945 gram gave 0.0407 gram V_2O_5 = 5.12 per cent.

These analyses correspond to the formula

$$18MoO_3.V_2O_5.8(NH_4)_2O + 15Aq.$$

		Calculated.	Found.	
$18MoO_3$	2592	74.89	75.22	
V_2O_5	183	5.29	5.12	
$8(NH_4)_2O$	416	12.02	11.99	12.18
$15H_2O$	270	7.80	7.58	
	3461	100.00		

A more extended investigation will, undoubtedly, show that the vanadio-molybdates are, to say the least, numerous. The salts which I have described are sufficient to establish a parallelism between them and the phospho-molybdates, which is the more interesting because the chemical relations of vanadium are nearer to antimony than to phosphorus and arsenic. I shall return to this point, however, in describing and discussing the class of antimonio-tungstates and antimonio-molybdates.

VANADIO-TUNGSTATES.

Vanadio-tungstates are very readily formed under conditions precisely the same as those which determine the formation of vanadio-molybdates, and which it is unnecessary to recapitulate. As a class they have a yellow, orange, or orange-red color. They are, so far as examined, readily soluble in water, are crystalline and extremely stable in composition, in the sense at least that it is often difficult to separate the combined vanadic and tungstic oxides, though in many cases complex salts easily break up into compounds of simpler type.

Analytical Methods.—When alkaline vanadates and tungstates are simply mixed together under conditions which do not result in the formation of vanadio-tungstates, it is possible to effect the separation of the vanadic and tungstic oxides by means of a solution

of ammonic chloride, which, as is well known, precipitates ammonic meta-vanadate in colorless crystals nearly insoluble in a saturated solution of ammonic chloride. This method cannot be applied directly to the separation of the two oxides when combined, as in the vanadio-tungstates, but the difficulty can be overcome by either of the following methods. An excess of ammonia is to be added to the solution, which is then to be digested, or, if necessary, boiled until the liquid becomes colorless. By this process, which, however, does not always perfectly succeed, the vanadio-tungstate is resolved into a mixture of ammonic tungstate and meta-vanadate. In place of ammonia, sodic or potassic hydrate in excess may be employed, and frequently with advantage. After the resolution of the vanadio-tungstate, as indicated by the color of the liquid, ammonic meta-vanadate may be precipitated by boiling with an excess of ammonic chloride. From the cold solution completely saturated with ammonic chloride the meta-vanadate may be separated by filtration, and the vanadic pentoxide estimated in the manner already pointed out. A variation of this process, which may often be employed with advantage, consists in fusing the vanadio-tungstate with an excess of potassic or sodic carbonate in a platinum crucible. The fused mass must be boiled with a strong solution of ammonic chloride, a drop or two of ammonia being added from time to time to keep the solution distinctly alkaline. The ammonic meta-vanadate is to be separated and treated as above. In applying these methods it is important in each case to be sure that the vanadium is exclusively in the form of pentoxide. It is therefore always advisable to add a little bromine water to the solution of the vanadio-tungstate before adding the excess of ammonia. In fusing with alkaline carbonates a little potassic or sodic nitrate may be added to the mixture in the crucible. In this manner we may avoid the error which would result from the presence of vanadic dioxide in the small quantity which often exists in consequence of the reducing agency of dust or traces of organic matter.

After a great number of trials, the methods given above are the only ones by which I have found it possible to effect even an approximate separation of vanadic and tungstic oxides in combination.

In place of the actual separation of the oxides, it is much more convenient, and I believe also in general much more accurate, to employ the following process, which permits us to estimate vanadium quantitatively in presence of tungstic, as well as of various

other oxides. This process depends upon the fact that vanadic pentoxide, either free or in combination, when boiled with strong chlorhydric acid, evolves chlorine, which may be collected in a solution of potassic iodide. The iodine set free may then be estimated with great accuracy by means of sodic hyposulphite after adding a solution of starch.

The fact that vanadic pentoxide evolves chlorine on heating with chlorhydric acid was, so far as I have been able to find, first remarked by Mohr, who in his well-known work on volumetric analysis suggested as possible the method of determining vanadium which I have employed, without, however, testing it in any single case.

It is possible, in some cases at least, to determine vanadic pentoxide in the presence of tungstic oxide by titration with hypermanganate. To the solution of the substance containing both metals, phosphoric and sulphuric acids are to be added, and the vanadic pentoxide is then to be reduced to dioxide by means of sulphydric acid gas passed into the boiling solution until complete reduction is obtained. No appreciable quantity of tungstic oxide is reduced under these circumstances. The titration with hypermanganate may then usually, though not always, be executed, and gives a fairly good result.

Finally, the method of titration by ferrous salts may often be used with success. The details have already been given, and do not need to be repeated.

5 : 1 *Vanadio-tungstate of Ammonium.*—When 12 : 5 ammonic tungstate is boiled with a solution of ammonic meta-vanadate an orange solution is obtained, which on evaporation deposits orange-yellow crusts of indistinct crystals. The color of this salt is somewhat dull; it is not very soluble in cold, but soluble in boiling water, and may be recrystallised without sensible decomposition. The salt becomes greenish upon the surface when dried upon woollen paper, from a slight superficial reduction of the vanadic pentoxide. Of this salt—

1.0558 gram gave 0.1222 gram $(NH_4)_2O$ by titration = 11.57 per cent.

1.1873 gram lost on ignition 0.2922 gram = 24.61 per cent. H_2O and NH_3.

1.0558 gram gave by titration with $KMnO_4$ 11.09 per cent. V_2O_5.

The analyses lead to the formula

$$5WO_3.V_2O_5.4(NH_4)_2O + 13Aq,$$

or

$$5WO_3.V_2O_5.4(NH_4)_2O.2H_2O + 11Aq,$$

if we regard the acid provisionally as 6-basic, which requires:

		Calculated.	Found.
$5WO_3$	1160	64.99	...
V_2O_5	183	10.26	11.09
$4(NH_4)_2O$	208	11.65	11.57
$13H_2O$	234	13.10	13.04
	1785	100.00	

The percentage of vanadic oxide found is too high, but there can be no reasonable doubt as to the formula. I obtained the salt but once, and then in small quantity. The solution gives a dull yellow flocky precipitate with argentic and mercurous nitrates, and after a time a yellow crystalline precipitate with excess of potassic bromide. The ammonium salt is interesting as being probably the first term in a series. It corresponds to the phospho-molybdate

$$5MoO_3.P_2O_5.3(NH_4)_2O.3H_2O + 4Aq.$$

The following may serve as starting points for further investigation. When normal baric tungstate, WO_4Ba, is boiled for a long time with a solution of ammonic meta-vanadate, it is very slowly dissolved to an orange-yellow solution, which on cooling gives very beautiful square tabular deep red crystals mixed with excess of baric tungstate. 12 : 5 baric tungstate dissolves more readily in the meta-vanadate, and gives a bright orange-yellow solution, which on evaporation yields fine prismatic crystals. From the above it appears probable that the tungstates of the heavy metals, both neutral and acid, will yield vanadio-tungstates by boiling with alkaline vanadates, and possibly in this manner various new series of salts may be formed. The costliness of the material for this work has prevented a more thorough study on my own part.

10 : 1 *Vanadio-tungstic Acid.*—A solution of ammonic meta-vanadate dissolves tungstic oxide readily on boiling, giving a deep orange-yellow solution. After long boiling with an excess of the oxide, the clear deep orange filtrate gives, with a solution of chloride of trimethylammonium, on standing some hours, two distinct

kinds of crystals, which are respectively yellow and deep orange-red. There are therefore, apparently at least, two different salts formed in the solution of the tungstic oxide. The solution of the ammonium salt gave with baric chloride, after some hours, sharp octahedral crystals of a yellow salt, but slightly soluble even in hot water. In a second experiment, baric chloride gave at once a yellow fine-grained crystalline insoluble precipitate; but the precipitation was not complete. On boiling the mixture of oxides obtained by igniting ammonic meta-vanadate in air with 12 : 5 sodic tungstate, I obtained a greenish-orange solution. This was oxidised by boiling with nitric acid, when it became orange. On standing, the acid solution deposited a relatively large quantity of a sulphur-yellow crystalline body, which was but very slightly soluble in cold water, and required a large quantity of hot water for complete solution. This substance was drained upon the filter-pump, washed with cold water, and dried upon woollen paper. Of this preparation—

0.8331 gram lost on ignition 0.1188 gram = 13.42 per cent.
0.8331 gram gave 0.7192 gram $WO_3 + V_2O_5$ = 86.03 per cent.
0.9786 gram gave 0.8411 gram " = 85.95 per cent.
1.0846 gram gave 0.0718 gram V_2O_5 = 6.62 per cent.

The analyses correspond with the formula

$$10WO_3.V_2O_5.6H_2O + 16Aq,$$

which requires:

		Calculated.		Found.	
$10WO_3$	2320	80.53	86.88	80.30	86.92
V_2O_5	183	6.35		6.62	
$22H_2O$	378	13.12		13.08	
	2899	100.00			

I did not succeed in obtaining salts corresponding to the 10 : 1 acid above described by saturating the acid with alkaline bases, as mixtures of the acid with alkaline vanadates and tungstates were formed until the point of complete saturation was reached.

18 : 1 *Vanadio-tungstic Acid.*—The orange-yellow mother liquor from which the 12 : 1 acid separated gave on evaporation beautiful crystalline needles of a second acid, the formula of which is

$$18WO_3.V_2O_5.6H_2O + 30Aq.$$

Of this acid,

1.0343 gram lost on ignition 0.1342 gram = 12.97 per cent. water.
1.0343 gram gave 0.0363 gram V_2O_5 = 3.51 per cent.

1.2540 gram lost on ignition 0.1617 gram = 12.90 per cent.
The formula requires:

		Calculated.		Found.	
$18WO_3$	4176	83.40 } 87.05		83.55 } 87.06	
V_2O_5	183	3.65 }		3.51 }	
$36H_2O$	648	12.95	12.90	12.97	
	5007				

The sum of the two oxides is determined by difference, which is the most accurate method whenever applicable. In this, as in all the other vanadio-tungstic compounds analysed, the vanadic pentoxide was determined by boiling with chlorhydric acid in the manner already described. The crystals of the 18 : 1 acid are readily soluble in water, and may be recrystallised without decomposition.

The compounds which I have described appear to establish a complete analogy between the vanadio-tungstates and phosphotungstates already described. Rammelsberg[1] has described a salt which crystallises in beautiful brown-black cubo-octahedrons, and which he obtained by saturating a commercial sodic vanadate with acetic acid and evaporating spontaneously. According to his analyses, the salt has the formula

$$(NH_4)_2O.WO_3.3V_2O_5 + 6Aq.$$

I suspect that it contains VO_3 as well as V_2O_5. I did not succeed in preparing it by synthesis, employing pure VO_3NH_4 and $WO_4(NH_4)_2$. It may prove to be the type of an entirely new class of complex acids, and well deserves further investigation.

(To be continued.)

Contributions from the Chemical Laboratory of Harvard College.

XXXVI.—β-PHENYLTRIBROMPROPIONIC ACID.[2]

By Leonard P. Kinnicutt and George M. Palmer.

α-Phenyltribrompropionic acid and the products formed when this acid is decomposed by boiling water were briefly described

[1] Berichte der deutschen chemischen Gesellschaft, 1, 161.

[2] Communicated by the Authors, from the Proceedings of the American Academy of Arts and Sciences.

by one of us last year.[1] During the past winter the study of the β acid was undertaken, and it has been considered best to give at this time the results so far obtained, as the further investigation must be carried on in different relations.

β-Phenyltribrompropionic acid was obtained by the action of dry bromine on β-monobromcinnamic acid, this last having been prepared in the way previously described.[2]

By the action of bromine on β-monobromcinnamic acid, Glaser[3] obtained an acid, which he describes as melting during the absorption of the bromine and only solidifying again after several days. The melting point he found to be 45–48° C. The results obtained by us are very different. Perfectly pure β-monobromcinnamic acid melting at 120° C. was placed under a bell glass with the theoretical amount of bromine. Not the slightest indication of melting was observed, and after twenty-four hours the bromine was all absorbed. The acid so obtained was purified by crystallisation from chloroform and melted at 151° C. It is soluble in alcohol, ether, carbonic disulphide, chloroform, and benzol.

The analyses gave the following results:

1. 0.2711 gram substance gave 0.2788 gram CO_2 and 0.0454 gram H_2O.

2. 0.3845 gram substance gave 0.3912 gram CO_2 and 0.0702 gram H_2O.

3. 0.1894 gram substance gave 0.2769 gram AgBr.

4. 0.1839 gram substance gave 0.2696 gram AgBr.

Calculated for $C_9H_7Br_3O_2$.		Found.			
		1.	2.	3.	4.
C	27.9	28.04	27.73	...	...
H	1.8	1.86	2.00	...	...
Br	62.17	...	...	62.24	62.40

Decomposition of β-Phenyltribrompropionic Acid by Water heated to 100° C.

Twenty grams of the acid were placed in a flask with two hundred cubic centimeters of boiling water. Decomposition began immediately, a volatile oil separating out, which at the end of eight hours had for the greater part been carried over with the steam, leaving a clear liquid that on cooling deposited a white crystalline substance. On examination, the oil was found to be a dibromstyrol, the white crystalline substance the α-monobromcinnamic

[1] Kinnicutt, this Journal, **3**, 4. [2] *Ibid.* [3] Annalen der Chemie, **143**, 339.

acid, and a third substance, which remained in solution in the liquid, gave on analysis results corresponding very closely to those required for a phenyldibromlactic acid.

Dibromstyrol, $C_8H_6Br_2$.

The oil that was carried over by the steam was separated from the water by ether, and, after thorough washing to remove all traces of hydrobromic acid, the ether was distilled off. The oil thus obtained was of a light amber color, growing gradually darker, and giving off on long standing traces of hydrobromic acid.

It boils at 253–254° C. with slight decomposition, hydrobromic acid being formed.

The analyses of the oil, dried over sulphuric acid, gave the following results:

1. 0.2518 gram substance gave 0.3328 gram CO_2 and 0.0518 gram H_2O.

2. 0.3592 gram substance gave 0.4810 gram CO_2 and 0.0744 gram H_2O.

3. 0.2518 gram substance gave 0.3615 gram AgBr.

4. 0.3032 gram substance gave 0.4379 gram AgBr.

Calculated for $C_8H_6Br_2$.		Found.			
		1.	2.	3.	4.
C	36.64	36.02	36.50	...	...
H	2.29	2.26	3.20	...	...
Br	61.06	...	...	61.10	61.40

The properties of this oil correspond in all respects with those of the dibromstyrol obtained from the decomposition of the α-phenyltribrompropionic acid,[1] and it seems most probable that the two substances are not simply isomeric, but identical. This point, however, cannot be positively settled till a careful study has been made of the addition products of both compounds.

α-Monobromcinnamic Acid.

The nearly clear liquid from which the bromstyrol had been distilled was made slightly alkaline with sodic carbonate, and shaken with ether to remove the last traces of the oil. The solution was then evaporated to a volume of about one hundred cubic centimeters and acidified with dilute hydrochloric acid. A white precipitate was thrown down, which after one crystallisation from boiling water melted at 132° C., and proved to be the α-monobromcinnamic acid.

[1] Kinnicutt, this Journal, 3, 4.

Two bromine determinations gave the following results:

1. 0.1986 gram substance gave 0.1661 gram AgBr.
2. 0.2242 gram substance gave 0.1874 gram AgBr.

Calculated for $C_9H_7BrO_2$.		Found.	
		1.	2.
Br	35.25	35.58	35.56

The barium salt, formed by adding baric chloride to a dilute solution of the acid in warm water, resembled in every respect the barium salt of α-monobromcinnamic acid as described by Glaser.[1] It was only slightly soluble in cold water and insoluble in alcohol. The barium salt of the β-bromcinnamic acid is hygroscopic, and soluble in alcohol.

The salt gave on analysis the following result:

0.3092 gram substance gave 0.1233 gram $BaSO_4$.

Calculated for $(C_9H_6BrO_2)_2Ba$.	Found.
Ba 23.23	23.42

The formation of the α-monobromcinnamic acid from both the α- and β-phenyltribrompropionic acids was rather to be expected, as Glaser has found that the β-monobromcinnamic acid is changed into the α by distillation, or by heating it with hydriodic acid,[2] and, moreover, Barish has shown that from both the α and β acids only the ethyl ether of the α acid can be obtained.[3]

Phenyldibromlactic Acid.

On evaporating the filtrate from the α-monobromcinnamic acid to a small volume, a substance crystallised out that melted at about 180° C. After recrystallisation several times from water, the melting point rose to 184° C., and it gave on analysis amounts of carbon, hydrogen, and bromine corresponding to those required for a phenyldibromlactic acid.

The acid is very soluble in water, alcohol and ether, soluble in chloroform, and slightly soluble in carbonic disulphide and benzol.

We have not as yet succeeded in obtaining the acid in large enough quantities to study its salts, or to decide which of the several possible formulae correctly represents its structure.

The analyses gave the following results:

1. 0.1854 gram substance gave 0.2257 gram CO_2 and 0.0440 gram H_2O.

[1] Annalen der Chemie, **143**, 334. [2] *Ibid.* 336. [3] Jour. für prakt. Chemie, **128**, 185.

2. 0.1989 gram substance gave 0.2440 gram CO_2 and 0.0470 gram H_2O.

3. 0.1605 gram substance gave 0.1870 gram AgBr.

4. 0.1812 gram substance gave 0.2122 gram AgBr.

Calculated for $C_9H_8Br_2O_2$.		Found.			
		1.	2.	3.	4.
C	33.34	33.21	33.42	...	...
H	2.46	2.63	2.62	...	...
Br	49.37	...	...	49.60	49.70

Action of Bromine on Dibromstyrol.

The dibromstyrol obtained from the decomposition of the β-phenyltribrompropionic acid was placed under a bell glass, with an excess of bromine. The oil gradually thickened, and after two days had absorbed about its own weight of bromine. It was then placed over quicklime, and after remaining there three or four days was washed thoroughly with water, and then separated from the water by shaking with ether. The so purified oil gave on analyses the following amounts of bromine:

1. 0.2050 gram substance gave 0.3646 gram AgBr.

2. 0.2110 gram substance gave 0.3737 gram AgBr.

3. 0.2055 gram substance gave 0.3651 gram AgBr.

Calculated for $C_8H_4Br_4$.		Found.		
		1.	2.	3.
Br	75.82	75.68	75.34	75.60

The substance is evidently a tetrabromstyrol. It is a thick viscous oil, soluble in alcohol, ether, and carbonic disulphide. It begins to decompose on heating at a comparatively low temperature.

It is to be hoped that the study of the products formed by the action of boiling water or dilute alkalies on the above compound, and also on the substance obtained by the addition of bromine to the dibromstyrol formed from α-phenyltribrompropionic acid, will not only show the structure of the two dibromstyrols, but will also give a more direct proof of the structure of the two monobromcinnamic acids than that obtained by Schotten.[1]

[1] Berichte der deutschen chemischen Gesellschaft, **15**, 1947.

XXXVII.—THE VOLUMETRIC DETERMINATION OF COMBINED NITROUS ACID.

By Leonard P. Kinnicutt and John U. Nef.

The amount of nitrous acid contained in commercial samples of potassic and sodic nitrites has been commonly determined in the following manner. The nitrites are dissolved in slightly acidulated water; a solution of potassic permanganate is added till the oxidation of the nitrous acid is nearly completed; the solution is then made strongly acid, and potassic permanganate added until the solution has a faint red color.

This method is far from satisfactory, closely agreeing results being rather the exception than the rule. The cause is most probably due to the escape of a small amount of nitrous acid, and also to the slow oxidation of the last traces of the nitrous acid by the potassic permanganate.

A further study of the analyses of nitrites volumetrically seemed desirable, and after numerous experiments the following process, or modification of the old process, as it might more properly be called, was devised.

The sample of nitrite is dissolved in cold water, one part of the salt to at least three hundred parts of water. To this solution a deci-normal solution of potassic permanganate is added, drop by drop, till the liquid has a decided and permanent red color, then two or three drops of dilute sulphuric acid, and immediately afterwards an excess of the potassic permanganate solution. The liquid, which should now be of a dark red color, is made strongly acid with sulphuric acid, heated to boiling, and the excess of potassic permanganate determined by means of a deci-normal solution of oxalic acid.

Analyses of samples of both potassic and sodic nitrites, made in accordance with the above modification, show that results agreeing very closely with one another can easily be obtained.

Potassic Nitrite Solution.

[One litre contained 4.3550 grams.]

Taken.	KNO_2 found.
25 cc. = 0.1089 gram	0.09194 gram = 84.44 per cent.
35 cc. = 0.1525 "	0.1289 " = 84.48 "
40 cc. = 0.1742 "	0.1472 " = 84.51 "
55 cc. = 0.2395 "	0.2024 " = 84.49 "
60 cc. = 0.2613 "	0.2210 " = 84.53 "

Sodic Nitrite Solution.

[One litre contained 3.090 grams.]

Taken.	$NaNO_2$ found.
25 cc. = 0.0919 gram	0.07713 gram = 83.95 per cent.
35 cc. = 0.1287 "	0.1082 " = 84.07 "
45 cc. = 0.1654 "	0.1390 " = 84.05 "
53 cc. = 0.1949 "	0.1639 " = 84.03 "
60 cc. = 0.2206 "	0.1854 " = 84.05 "

The volumetric method for the determination of sulphites is also most unsatisfactory. The study of this subject was therefore given to Mr. R. Penrose, a student in this laboratory. He experimented both with potassic permanganate and oxalic acid as above, and also with iron alum and the permanganate; but, although many variations of these processes were tried, and the work carefully conducted, the results were not satisfactory.

Communications from the Chemical Laboratory of Rutgers College.

XII.—THE PURIFICATION OF AMMONIUM FLUORIDE.

By Peter T. Austen and Francis A. Wilber.

One of the most convenient methods of determining silica in titaniferous and other ores is to expel it as fluoride by means of ammonium fluoride and sulphuric acid, or by fluorhydric acid alone. But the practical difficulty here met is the impossibility of getting either ammonium fluoride or fluorhydric acid in a pure state, for it is of course absolutely necessary that they should leave no residue after volatilisation. The following procedure has enabled us to use the articles obtainable in commerce with excellent results.

The amount of ammonium fluoride necessary for the analysis is dissolved in as little water as possible in a platinum dish, and strong ammonia added in slight excess. If fluorhydric acid is used the ammonia is added in small amounts from a pipette, so as

to avoid spitting. In this case the operation is of course performed under a good hood. In both cases a voluminous precipitate will be obtained. A five-inch filter paper, which has previously been extracted[1] with fluorhydric acid to remove silica, is folded to the sixteenth fold, making a cone of an angle of about 67°. If the papers are very thin it is well to take two of them and fold them together. This cone is then placed in a ring of stout platinum wire, which may be conveniently held in the ring of a ring-stand by three smaller platinum wires. The liquid is decanted into this filter and allowed to filter at once into the platinum crucible containing the ore. The crucible is then placed on a water-bath and the liquid concentrated. This step is not necessary unless the bulk of the liquid is large or the crucible small, and indeed had better be avoided, since ammonium fluoride is quite volatile. The liquid is next made acid with sulphuric acid, evaporated to dryness and ignited as usual. Should it be feared that the silica had not been entirely expelled, the operation should be repeated, but it will be found that as a rule one treatment is sufficient. The ammonium fluoride prepared in this way we find does not leave any appreciable residue. Of course every new lot of ammonium fluoride or fluorhydric acid, before being used in analysis, should be tested for residue after treatment in this manner.

We prefer to use the acid in analysis, purifying it and converting it into the ammonium salt by the above method, for its cost is but one-third of that of the ammonium fluoride and it affords a more concentrated solution.

NEW BRUNSWICK, N. J.

[1] Papers freed from ash by treatment with chlorhydric and fluorhydric acids are now manufactured by Schleicher and Schüll by a method described by me in 1878 (Chemical News, **37**, 149) and tested and approved by Profs. Fresenius and Caspari (Zeitschrift für analytische Chemie, **22**, 241).—P. T. A.